

*Office of the Quartermaster General
Military Planning Division
Research and Development Branch*

FLAMEPROOFING TEXTILE FABRICS

*Prepared by a Staff of Specialists
under the Editorship of*

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Major, Q.M.C.

*under Research Project Q.M.C. #27
of the National Research Council
National Academy of Sciences*

American Chemical Society
Monograph Series



REINHOLD PUBLISHING CORPORATION

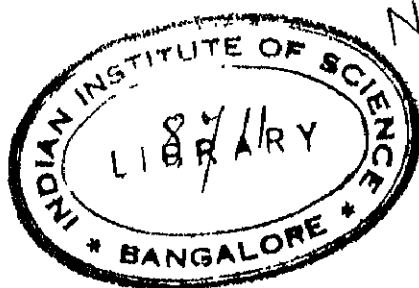
330 West Forty-second Street, New York, U.S.A.

1947

Released for public information
by
The Office of the Publication Board
U. S. Department of Commerce

540-0202

N21-104



Printed in United States of America by
BERWICK & SMITH CO., NORWOOD, MASS.

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General Introduction

American Chemical Society Series of
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By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic monographs on chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, secretary of the society, Washington, D. C.; the late John E. Teeple, then treasurer of the society, New York; and the late Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the A.C.S. series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successors) of New York.

The Council of the American Chemical Society, acting through its Committee on National Policy, appointed editors (the present list of whom appears at the close of this introduction) to select authors of competent authority in their respective fields and to consider critically the manuscripts submitted.

The first monograph of the series appeared in 1921. After twenty-three years of experience certain modifications of general policy are indicated. In the beginning there still remained from the preceding five decades a distinct though arbitrary differentiation between so-called "pure science" publications and technologic or applied science literature. This differentiation is fast becoming nebulous. Research in private enterprise has grown apace and not a little of it is pursued on the frontiers of knowledge. Furthermore, most workers in the sciences are coming to see the artificiality of the separation. The methods of both groups of workers are the same. They employ the same instrumentalities, and

now frankly recognize that their objectives are common, namely the search for new knowledge for the service of man. The officers of the Society therefore have combined the two editorial Boards in a single Board of twelve representative members.

Also in the beginning of the series, it seemed expedient to construe rather broadly the definition of a monograph. Needs of workers had to be recognized. Consequently among the first one hundred monographs appeared works of the form of treatises covering in some instances rather broad areas. Because such necessary works do not now want for publishers, it is considered advisable to hew more strictly to the line of the monograph character which means more complete and critical treatment of relatively restricted areas, and where a broader field needs coverage, to subdivide it into logical sub-areas. The prodigious expansion of new knowledge makes such a change expedient.

These monographs are intended to serve two principal purposes: first, to make available to chemists a thorough treatment of a selected area in form usable by persons working in more or less unrelated fields to the end that they may correlate their own work with a larger area of physical science discipline; second, to stimulate further research in the specific field treated. To implement this purpose the authors of monographs are expected to give extended references to the literature. Where the literature is of such volume that a complete bibliography is impracticable, the authors are expected to append a list of references critically selected on the basis of their relative importance and significance.

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Foreword

The pressing demands of war have always served as a stimulus to research and development in the field of Science. The recent conflict, coming as it did at the time of our entrance into what has been termed the "Age of Science," imposed particularly heavy demands upon the technical ability of our scientists to discover and develop new instruments of warfare and corresponding protective devices.

Our early experiments focused attention upon the desirability of developing suitable methods for rendering military fabrics resistant to flame propagation. A preliminary survey of existing flame-retardant treatments indicated the need for basic research on the general subject of flameproofing. Research has been defined as: "studious inquiry; usually, critical and exhaustive investigation or experimentation having for its aim the revision of accepted conclusions, in the light of newly discovered facts." In nearly every instance the problems facing the Armed Services were approached along the avenues of research in the firm belief that herein lay the quickest and most satisfactory solution. Certainly, in the search for suitable methods of flameproofing cotton fabrics intended for military usage, a thorough understanding of the fundamental mechanisms involved has led to a wholesome revision of previous concepts and a clearer recognition of the potentialities of available processes. In addition to meeting specific military needs, the researches conducted represent the first extensive study of the fundamentals of flameproofing and have laid a firm foundation upon which future investigations may be based. The success of the research programs undertaken is attributable to the cooperation and perseverance of those actively engaged therein, both in civilian and military capacities.

In agreement with the proposition of Thomas Hobbes, that "the main purpose of science is the tying of facts into bundles," it was felt that the experiments performed and the findings thereof should be collected and presented to the interested public. With that in mind, this monograph on "Flameproofing Textile Fabrics" was prepared

GEORGES F. DORIOT
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Office of the Quartermaster General
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Washington, D. C.
March, 1947



Preface

The need for practical methods of combating fabric inflammability was brought forcibly to the attention of many branches of the Armed Services upon our entry into World War II. Programs were initiated in many service laboratories with the intention of investigating the practical application of flameproofing treatments to various military fabrics.

Initially, Quartermaster Corps activities in the field of flameproofing were concentrated upon the application of flame-retardant finishes to tentage duck. At the same time, similar programs dealing with the flameproofing of fabrics were in progress in other service laboratories. The Army Corps of Engineers at the Engineer Board, Fort Belvoir, Virginia, was engaged in the development of commercial as well as field impregnation methods for the treatment of camouflage netting. The Navy at the Industrial Test Laboratory, Naval Shipyard, Philadelphia, Pennsylvania, pursued a similar investigation of the flameproofing of life jackets. The Chemical Warfare Service Development Laboratories at the Massachusetts Institute of Technology, Cambridge, Massachusetts, investigated suitable methods for the flameproofing of summer flying suits for Air Corps personnel. During the North African campaign it became apparent that fire-resistant finishes should be available for general use on clothing fabrics.

In view of the fundamental nature of the research which it was evident would be required to attain a satisfactory solution of this problem, the Research and Development Branch, Military Planning Division, Office of the Quartermaster General, requested the National Academy of Sciences to initiate a research program. Accordingly, in October, 1943, the National Research Council of the Academy contracted with Columbia University for the establishment of a research project in the Department of Chemical Engineering on the subject "The Flameproofing of Army Clothing."

The results of these researches, conducted over a period of a little less than three years, are being made available to the general public in this volume. In addition, the report includes a great deal of related information on the general subject of flameproofing which was obtained through other Quartermaster Corps programs and research projects in other service laboratories.

It is believed that making this information generally available will stimulate further research in the field, particularly that of a more fundamental nature. Furthermore, it will greatly advance the knowledge of

other investigators working along the same lines. In this way, it should be possible to obtain, within a relatively short time, even better flame-retardant finishes for military fabrics than are known today as a result of wartime researches.

It was felt particularly desirable to publish this volume at this time in order that the results of the various investigations might be recorded soon after completion of the experimental programs and to avoid any possibility that the information would not be disseminated in a consolidated form. Furthermore, recent legislation pertaining to the fire hazard of textiles now under consideration in various state legislatures as well as in Congress emphasizes the importance of making this material available as a matter of public safety.

The subject matter of this book has been presented as a comprehensive survey of the subject of flameproofing textile fabrics rather than in the form of a technical report of the investigations carried out. The material has accordingly been divided into three general sections which consider in turn the fundamental mechanisms of the thermal degradation of cellulose and the chemical or physical phenomena of flameproofing; the methods employed in the processing and evaluation of flameproofed fabrics; and the various applications which exist for flame-retarding treatments in the field of textile fabrics. This type of presentation should enable the reader to become familiar with the types of retardants available, the function of these agents in the prevention of flaming and glowing, and the methods by which they are applied and evaluated before attempting to appreciate the differences in performance when applied to fabrics.

Chapter I serves as an introduction to the subject of flameproofing. An attempt has been made to clearly define the objectives of flameproofing treatments, the requirements which might be set up for an ideal treatment, and the variables influencing the effectiveness of a flameproofing agent. A glossary of terms has also been included with the intention that the confusion which currently exists in the nomenclature employed in discussions of flameproofing would be avoided, at least in the interpretation of the subject matter of this volume.

In Chapter II, the nature of cellulose is reviewed briefly followed by a thorough discussion of its normal degradation reactions. It was thought that this background was necessary in order to attack the more complex problem of high temperature degradation. The reader is then introduced to the thermal degradations of cellulose at elevated temperatures and the nature of the decomposition products obtained. The influence of flame-retardant materials upon the formation of these products is proposed as one of the primary effects of flameproofing.

The fundamental causes of the prevention of both afterflaming and afterglow are considered in Chapter III. In this case the mechanisms which have been commonly proposed in the literature on the subject are

presented along with more recent theories which possess a firmer foundation in experimental fact.

The purpose of Chapter IV is to thoroughly acquaint the reader with the test methods commonly employed in the evaluation of flameproofed fabrics. In some cases, the tests described are specific for fabrics intended for military purposes and would not be widely applicable in the textile industry. Many of the tests included, however, have been developed or improved in the course of war research projects and may warrant a more widespread usage.

Chapter V is intended to present a survey of the general types of treatments available, the variables which exist in the application of these agents to the fabric, and the industrial processing techniques employed in commercial practice. The value of this section has been enhanced by the inclusion of adequate experimental data to illustrate the effects of the variables discussed.

In Chapter VI, the relative efficiencies of many of the better available treatments are compared in regard to their suitability for use in the processing of military uniforms. The criteria employed include not only laboratory evaluation techniques but also practical wearing tests.

A similar comparison of flameproofing treatments and their applicability for use on military fabrics other than articles of clothing is made in Chapter VII. Included in this group is a consideration of flameproofed tentage fabrics which probably represent the principal application of flame-retarding treatments in the textile industry to date.

The final chapter on civilian applications (Chapter VIII) points to the need for an effective and durable flameproofing treatment. In addition, current restrictions and proposed legislation are discussed along with the question of implied warranty.

The book includes as many of the different flameproofing treatments and as much of the available data as could conveniently be considered. An attempt has been made to group the flameproofing agents according to the manner of their performance and select the data which would best illustrate the points discussed.

Though the publication of information of this type in the form of a collaborative volume possesses many obvious disadvantages, the scope of the subject matter as originally envisioned and the time allotted for completion made it highly impractical for any one person to write the book in its entirety. Furthermore, since the experimental work described was carried out in several different government and industrial laboratories, having one of the individuals closely connected with the original investigation contribute the write-up of the experiments performed helps to insure that valid conclusions are drawn on the data obtained and serves as an acknowledgment of the contributions of the individual or organization.

The selection of authors was generally made on the basis of those best

qualified and at the same time best able to submit their contributions within the allotted time. In many cases the task was difficult since many of the individuals considered were already overburdened with the responsibilities of their regular positions. The response to the invitations was gratifying, however, and those who refused were prompted to do so by the pressure of previous commitments.

Since the majority of the work described was performed under government contracts and many of the contributors were in the employ of various government agencies, it was felt to be improper to allow royalties to accrue to the authors. Instead, all royalties have been applied to a reduction in the purchase price of the book. This is wholly in accord with the original objective of making the subject matter available to the greatest number of interested persons.

The editor wishes to express his sincere appreciation to the several authors. In every instance they cooperated to the full extent of their ability despite other heavy demands upon their time. In addition, I am deeply indebted to the members of the editorial board who were mutually charged with the organization of the subject matter and selection of authors as well as the editing and compiling of the manuscript itself. Without the cooperative effort of this group the task would have been all but impossible.

Special appreciation is due Miss Charlotte Yater whose familiarity with the subject matter considered rendered her particularly suited to the task of preparing and compiling manuscripts and also assisting in the reading of proof.

The preparation of the subject index was carried out by Miss Cynthia Berlow.

Graphs and illustrations in the text were prepared by Prof. Frank H. Lee of Columbia University.

Grateful acknowledgments are extended to the many others who have contributed to the preparation of this book in any way and to those individuals to whom we are all indebted for carrying out the actual laboratory investigations. Special mention should be made of Dr. Milton Harris, Dr. M. W. Sandholzer, and Mr. K. S. Campbell who contributed advice and criticism on the contents of some sections.

Further acknowledgments are also due to many individuals in the Research and Development Branch of the Office of the Quartermaster General and to the National Research Council Committee on Quartermaster Problems of the National Academy of Sciences for their interest and cooperation.

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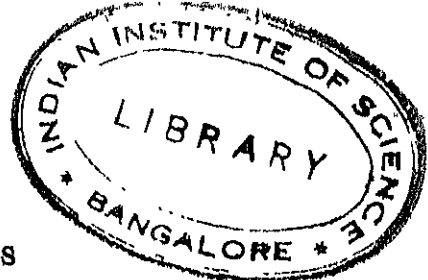
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Section One

FUNDAMENTALS





Chapter I

Flameproofing Defined

James M. Church

Development of Flameproofing. Ever since the beginning of man, he has been actively engaged in seeking improvements in his existence both from a personal standpoint as well as in the interest of the welfare of others. Included in man's pursuit of happiness down through the ages has been his persistent search for some means of combating fire, which has destroyed some of his most priceless possessions and at times has left him destitute, causing loss of life, home and property. During the advance of the civilization of man we note his progress in this respect, mainly through methods of control. The first attempts were confined to the development and use of materials which would withstand the action of fire and have finally culminated in the construction of our present-day fire-proof buildings and structures. Of the many fire-resistant materials discovered and perfected by man, none have been found suitable for protection in the form of clothing. The natural fibers which have been used for ages, spun and woven together into fabrics, are all combustible to varying degrees, but otherwise possess those characteristics of warmth, wear, flexibility and beauty which are paramount for clothing purposes. With the advent of man-made fibers, it has been the aim of the scientist to perfect the ideal fiber which also includes the desired fire-resistant qualities. In some respects this has been accomplished to the extent of developing synthetic fabrics of much greater resistance to fire than some of those made from natural fibers.

The recent world war with its holocaust of destruction by fires originating from incendiaries, flame throwers and the use of highly combustible fuels brought about a greater renewed effort by the scientists to find better means of protection against fires which cause ignition of the clothing and result in burn casualties. The modern type of warfare with its mechanized armored machines brought with it new dangers to the military personnel, which in the early days of the war resulted in high loss of life and disabilities.

The results of scientific researches carried out during war times for the protection of military personnel inevitably find ready uses in the peacetime civilian life to follow. This will undoubtedly be true in the case of

flameproofing. Local, state and federal legislation in the interest of public safety are already demanding greater fire protection from the use of clothing and interior fabrics, in order to avoid the calamities which are reported almost daily in the press due to injuries sustained from fires originating from combustible fabrics. In this modern scientific age man is now prepared to offer some definite solution to this perplexing problem, by incorporating with the fibers chemicals which will greatly retard their combustibility and thus prevent ignition of the fabric.

What Is Flameproofing? The term "flameproofing" would imply the employment of some method to prevent the ignition of a combustible material, thus restricting its destruction by flame. However, throughout the literature on this subject, there is still considerable confusion between such terms as "fireproofing," "flameproofing," "flame-resistant," "non-glowing," etc., even to the extent of using some of these interchangeably. Since there exist degrees of combustibility of materials, it would seem best to define these in a general way to limit the degree of combustion within a specified range. When describing a material as "fireproofed," the use of this term should convey the meaning of total resistance to destruction by fire and should not be used with any of the lower fire-resistant types of materials. Likewise in the case of a material which does not withstand the action of fire without some change in its physical state, but does prevent self-combustion once the igniting source has been removed, the term "flameproofed" would be applicable in its description. The lesser fire-resistant materials which do not burn too readily may likewise be characterized as "flame-resistant."

One characteristic of cellulosic materials different from most combustibles is their tendency to be consumed, after the flame has been extinguished, by a glowing, non-flaming type of combustion. This raises the question in characterizing the inflammability of combustible types of cotton goods whether one should not differentiate between flaming and the glowing tendencies during combustion of the fabric. In the case of certain flameproofing treatments which have been applied to the fabric in order to reduce its susceptibility to combustion, it is possible to render the cloth fairly flame-resistant and yet it will be consumed by an afterglow which persists even after the source of the heat or flame has been removed. In some respects this afterglow may prove to be of more serious consequence than the flaming usually associated with fires. The heat resulting from afterglow is in most cases more intensive than the flame, resulting in serious damage and injury, besides the possibility that it might produce renewed flaming. Therefore in the use of the term "flameproofing" as applied to fabrics, it should imply not only resistance to continued flaming but also include the absence of any afterglow. In other words, both non-flaming and non-glowing should be included in the term "flameproofing" when used to characterize any cellulosic or other material capable of

being consumed by a glowing type of combustion. For a practical use of this term, in evaluating such materials, it is desirable to define the amount of afterflaming and afterglow, rather than attempt to make its use limited to those materials which exhibit absolutely no tendency toward either, since in most instances a slight amount is evident but does not persist for any appreciable time.

Furthermore, in carrying out flame test measurements of fabric combustibility, the recognition of a slight afterflame or afterglow is often dependent upon the person performing the test. A flame or glow of a fraction of a second's duration is often confused with optical after-images or with the light emanating from the incandescent carbon filaments during the brief cooling period. The latter phenomenon should not be confused with the progressive, exothermic oxidation of the char.

For these reasons a fabric is regarded as flameproofed if it shows no afterflaming of a measurable amount, and no afterglow in excess of four seconds after the flame has ceased. To differentiate between fabrics which may be resistant to one but not to the other, the terms "flame-resistant" and "glow-resistant" may be applied individually, but should be further characterized by denoting, in terms of seconds' duration, the degree of resistance offered in both respects.

Classification of Flame Retardants. Since flameproofing agents are chemical substances it is only natural that any attempt at a classification would include a grouping according to similarities in their chemical structure. This would permit listing various types of phosphates, sulfates, borates, sulfamates, salts of zinc, antimony, tin, or other similar compounds together for a convenient chemical classification. This, however, is found to be of little use from a practical standpoint since various compounds of the same type behave entirely differently as fire retardants. This is brought out forcibly in the comparison of the various phosphates, which in the case of the weaker basic salts are efficient flameproofing agents but with the stronger basic salts such as tri-sodium phosphate or the more insoluble metallic phosphates the latter are very ineffective.

From the preceding discussion of the terms to be applied in characterizing the degree of flameproofing to be obtained by the use of various retardants, one might be inclined to group the flameproofing agents into classes according to whether they exhibit complete flame and glow-retarding tendencies, or perhaps only a partial flame and glow resistance. Such a classification leads to confusion in borderline cases of retardants which under some circumstances may be effective flameproofing agents when employed in certain combinations, but which under less favorable circumstances offer only a weak resisting action toward the combustion of the fabric by flame or glow. Unless a close distinction is permitted in the requirements set up for the various classes, it would be likewise rather difficult to determine whether a given retardant is of the "flameproofing" or

the "flame-resistant" type, in such borderline cases. Therefore any classification based upon the performance of a flame-retardant chemical must be restricted to a general grouping and as such becomes useful in characterizing the various agents according to whether they possess good flameproofing or glowproofing qualities or whether they are of the milder type of flame-resistant or glow-resistant agents.

One of the most useful classifications for a practical flameproofing of textile fabrics is one which is not based on their relative effectiveness, but rather upon their durability in offering continued resistance to the inflammability of the fabric during its use. Any worthwhile commercial treatment would require not only an initially effective flameproofing but one which would be capable of some resistance toward any action tending to remove it or destroy its effectiveness. Such a classification would permit listing the different flameproofing agents or treatments as either (1) temporary, (2) semi-durable, or (3) permanent. The first class would include the water-soluble retardants, which for the most part are highly efficient but are readily removed by a simple immersion in water, thus destroying their effectiveness. The second class, on the other hand, would include those capable of withstanding the action of a water leach but which are easily removed or destroyed by stronger solutions of salt or soap as encountered in sea water immersion or laundering operations. The last and more durable type are those agents which will resist the action of the stronger leaching solutions within a reasonable degree and therefore, with certain precautions as to the severity of the treatment, can be depended upon to offer continued protection to the fabric in preventing complete combustion by flame. Standard leaching tests are now available for evaluation of the various flameproofing agents according to their permanency as defined above. This is accomplished by merely limiting the type of leaching solution for the three classes to (1) ordinary tap water, (2) dilute salt and mild neutral soap solutions, and (3) common commercial soap solutions as employed in commercial laundering practice. The exact conditions of each leaching test can be readily defined in terms of temperature and duration of leach required before effectiveness of the flameproofing is impaired.

Further considerations of a suitable classification of flame retardants might well include some specification of requirements based upon the effectiveness obtained from a given amount of the chemical, or the reverse in terms of the quantity of retardant necessary to produce a given degree of flameproofness. The latter is perhaps the most convenient standard to adopt since it offers a suitable comparison of the relative effectiveness of the various agents on a weight or per cent add-on basis. Minimum requirements for effective flameproofing agents can therefore be established in terms of the add-on required to produce a minimum afterflaming, afterglow and resulting char area as measured by the standard flame tests.

Formerly, the flame test requirements for treated fabrics in general allowed for a short two-second afterflaming and a maximum char length of 3.5 inches but no measurement of afterglow was made. More recent developments, particularly in the adaptation of flameproofing treatments to clothing fabrics, where the performance requirements might well be more severe, have necessitated raising the flame test specifications.

In the case of the Vertical-Bunsen burner flame test the standard requirements for acceptable treatments have now been established as (1) no afterflaming, (2) less than 4 seconds' afterglow, and (3) less than 3.5 inches of char length. In adhering to this specification in adopting the 45°-Microburner flame test as the preferred standard, the requirements on a comparative basis would be much the same, namely, (1) no afterflaming, (2) less than 4 seconds' afterglow, and (3) less than 2.5 square inches of char area. The quantity of retardant required for the treatment of a fabric to meet the above flame test specifications might then be considered as the "minimum effective add-on" and could be used for comparative purposes in the evaluation of flameproofing agents.

Other Factors Affecting Flameproofing Efficiency. In addition to the effectiveness of the fire retardant as discussed in the foregoing section, there are several other factors which greatly affect the efficiency of the flameproofing treatment. The first of these is the type and structure of the fabric to be treated. The majority of the considerations of this volume have been confined to the flameproofing of cellulose fabrics. This type of fabric constitutes the great majority of the textile fabrics either in the form of cotton goods or the regenerative type of rayon. Furthermore, cellulose is one of the more combustible types of fiber and would therefore warrant more serious considerations of possible methods of flameproofing than perhaps most of the other fibers. However, this does not preclude the possibility that many of the treatments discussed here are equally applicable to fabrics woven from other natural or synthetic fibers. Since, however, the mechanisms governing flameproofing phenomena are concerned chiefly with chemical reactions involving pyrolysis and combustion, it is logical to conclude that changes in the chemical structure of the fiber might well radically alter either the rate or direction of the reaction and result in less effective flameproofing with a given retardant or treatment. For this reason the processing of other types of fabrics for an efficient flameproofing may present an entirely different problem which may or may not require a different method of approach for solution.

In similar fashion, variations in the weight and weave of the fabric introduce corresponding variables in application of effective flameproofing agents. In the case of cotton goods, these factors concern themselves mainly with the amount of retardant required and the conditions for application for an effective flameproofing treatment. This conclusion is based upon the fact that the components of cellulose and fire retardant are com-

mon to all types of cotton fabric, and if intimate contact of the two is obtained in the treatment, the underlying requirements of the flameproofing mechanisms are satisfied.

Another of the factors affecting the degree of flameproofness obtained from a given fire retardant is inferred in the above discussion. This is concerned with the conditions employed in the treatment of the fabric with the flameproofing agent. From a consideration of the mechanisms evolved for explaining flameproofing phenomena it would follow that the main object of any treatment should be to achieve a uniform and intimate distribution of the retardant within the fabric in close contact with the individual fibers. This is evident from the fact that the water-soluble agents afford a maximum degree of flameproofing with a minimum amount of retardant. Here the highly dispersed solution of the agent permits a complete and thorough distribution of the chemical within the fabric structure. In the case of the less soluble retardants, the large particle sizes very definitely limit the possibility of uniform and intimate distribution, and this is accountable, at least in part, for the fact that much greater amounts of these agents are required to obtain an equally effective treatment. Therefore thoughtful consideration should be given in the application of any chosen flameproofing agent to a given fabric which will include a selection of the best conditions and methods possible for the treatment in order to achieve this ultimate object. In many instances the only approach, with due regard to the physical properties of the flameproofing compound, is one of a systematic investigation of the variables to be encountered in the treatment or method by trial and error type of experimentation.

Most of the treatments and field tests reported here were made with an 8.5-oz. olive drab herringbone twill which constitutes a high percentage of military uniforms in the form of combat and fatigue suits and coveralls. In investigating the effects of the added ingredients of dye, sizing and extraneous matter occurring in the finished cloth it was found that these were mainly of a minor consequence in the effectiveness of the flameproofing agents, provided the treatment allowed for an intimate and uniform distribution of the agent. Actually in testing grey goods, dyed goods and sized fabrics, these ingredients were found to contribute slightly to the flameproofing qualities of the treated fabric. In other words, the natural pectin, wax or resin present in the original fabric, or the added dye and resin employed in the finishing of the fabric are in reality flameproofing agents of a low order. These substances, however, interfere in some instances with the effectiveness of the treatment by rendering the fabric less acceptable to the flameproofing agent. This is particularly true in the case of sizing components which in most cases should be removed by a preliminary desizing treatment prior to the flameproofing treatment in order to prepare the fabric in a more absorptive state. After the flame-

proofing treatment the sizing may be restored for effecting a finish to the cloth but should be applied in such a way as not to disturb the distribution of the flameproofing agent.

In many regards the 8.5-oz. desized herringbone twill offers an excellent type of cotton fabric for adoption as the standard for evaluation of flameproofing treatments. Its texture and weight may be considered as typical and representative of the majority of cotton fabrics for consumer use. It is therefore suggested that this type of cotton cloth be adopted as the standard testing fabric for all flameproofing specifications in evaluation tests.

Ideal Characteristics of Flameproofing. The most desirable flameproofing agent would be one which could be easily applied to a fabric, preferably in a finished form ready for use, and would render that fabric permanently flameproofed without appreciably altering the fabric characteristics for consumers' use. This definition of an ideal flameproofing agent might at first glance not appear too unreasonable but further analysis would show it to be highly idealistic in view of present-day facts concerning flameproofing. And yet it serves its purpose in presenting an ultimate specification for flameproofing, which will challenge those attempting improvements toward a more satisfactory solution of this problem. It is not wholly improbable that such a flameproofing agent may some day be discovered, for science does not recognize any situation as being impossible regardless of its difficulties. Only by means of a thorough understanding of the problem in all of its aspects will scientists of the future achieve this coveted goal, and it is to this purpose that the following discussion of the fullest meaning of these ideal specifications is dedicated.

Ease of application has been the one requirement, in addition to a high degree of effectiveness, that has made the water-soluble agents so popular, even though they are readily removed by the slightest leaching action and are apt to produce a deleterious effect to weaken the fabric strength. In terms of permanency, the better of the agents are the most difficult to apply, which would make it appear that ease of application and permanency do not go hand in hand. The requirement of durability includes many factors and is not confined to launderability alone although this factor has been of major importance. Permanency against the conditions of aging and storage and against the action of salt spray or salt water is sometimes more difficult to attain with certain agents than protection against laundering. Excessive humidity and temperature, as encountered in tendering tests, may tend to destroy the flameproofing treatment, as well as impair the strength of the fabric through the decomposing action of the agent. In the application of the more permanent types of flameproofing agents, it has been found necessary to employ an excessive amount of the retardant in order to obtain an effective treatment. In doing so, not only is the weight of the fabric increased appreciably but

usually the hand is greatly impaired. As might also be expected in such cases, excessive amounts of the treatment may affect the permeability of the fabric. In this regard both air and vapor transmission are important, otherwise clothing fabrics are certain to produce discomfort to the wearer by causing excessive heat loads for lack of proper heat transmission. In most cases of clothing fabrics, nontoxicity of the chemical retardant is a necessary prerequisite. Not only must the treatment not contain harmful chemicals but the treatment itself must not induce any harshness to the fabric finish which might cause a rash or dermatitis condition upon the skin of the wearer. Since textile fabrics for consumer use require other treatments and finishes, any acceptable flameproofing treatment must be compatible with the others. In the matter of efficient flameproofing from the use of chemical retardants, only those which will limit the inflammability of the fabric to the extent of no afterflaming and a minimum of afterglow can be regarded as of major importance. An added requirement might also include that the char resulting from the limited combustion of the fabric be of a substantial type which will contribute some protection against further exposure to the flame source. Such chars have been shown to offer a considerable degree of insulation.

In summary, the following requirements should be considered in the selection of any flameproofing agent or treatment:

1. A minimum effective add-on to avoid both an excessive increase in the weight of the fabric and the imparting of a poor hand to the fabric.
2. Means of easy application to the fabric, which may permit its use directly with garments or consumer goods.
3. A reasonable permanency of the treatment toward the leaching action of water, salt and soap solutions, and dry-cleaning solvents.
4. Freedom from any deleterious action upon storage or during conditions of use which may cause a decrease in the fabric strength through a tendering action.
5. No appreciable decrease in the permeability of the fabric as measured by both air and vapor transmission.
6. Compatibility of the treatment with other treatments used in the finishing of the fabric.
7. Avoidance of any physiological action of the retardant on the skin, both in the treatment and wear of the fabric.
8. A flameproofing efficiency which prohibits the propagation of any flame and any appreciable afterglow, resulting in a charred fabric which still retains considerable of its strength characteristics.

Glossary of Flameproofing Definitions. The following general terms, to be encountered throughout this volume, are listed here with their definitions for a ready reference and a better understanding of the full meaning of flameproofing as discussed in the following chapters of this book.

Add-on—Weight increase of fabric due to absorbed flameproofing agent or solution after treatment. Usually applied to the dry weight basis, otherwise termed "pickup."

Afterflame—The time in seconds which the fabric flames after the source of flame has been extinguished.

Afterglow—The time in seconds which the fabric glows after all flaming has ceased.

Char Area—The blackened area resulting after all flaming and glowing have ceased. Usually well defined and easily measurable by use of a planimeter.

Char Length—Used only in the Vertical flame tests and represents the furthest distance of the damage caused by flaming or glowing as measured from the originating point of the flame or lower edge of the fabric strip.

Combustion—Chemical decomposition caused by a combination of the substances with oxygen causing evolution of light and heat in a burning reaction.

Fabric Weight—Expressed in ounces per square yard.

Fill—Threads of the weave of a fabric which are at right angles to the selvage.

Flame Retardant—A material which imparts resistance to afterflame to the fabric.

Flame Test—Standard procedures employing different types of flame for testing the flameproofness of a fabric.

Flameproofed Fabric—A treated fabric which exhibits appreciable resistance to both afterflame and afterglow in the standard flame tests

Flameproofing Agent—A material which imparts resistance to both afterflame and afterglow to the fabric.

Flame-resistant Fabric—A fabric treated as to inhibit afterflaming in the standard flame tests.

Glow-resistant Fabric—A fabric treated as to inhibit afterglow in the standard flame tests.

Glow Retardant—A material which imparts resistance to afterglow to the fabric.

Heat Load—Excessive accumulation of body heat. Usually measured by increase in sweat rate, pulse, and body temperature.

Herringbone Twill—A weave characterized by diagonal lines produced in a ribbon effect by a series of floats or skipped threads staggered in the direction of the warp.

Minimum Flameproofing Requirements—A treatment which provides no afterflame, less than 4 seconds' afterglow, and char length or char area of less than 3.5 inches or 2.5 square inches respectively by the Vertical-Bunsen burner and the 45°-Microburner tests.

Pickup—Weight increase of a fabric following treatment. Usually employed for a wet weight increase.

Pyrolysis—Chemical degradation caused by the action of heat. May be accompanied by combustion if carried out in the presence of air.

Sizing—Any added material which imparts body to a yarn or fabric.

Tendering Action—Any effect of the chemical agents used in the treatment of a fabric, or conditions of exposure of the fabric which will result in loss of fabric strength.

Warp—Threads of the weave of a fabric which are parallel to the selvage edge.

Chapter II



Degradation of Cellulose

Prior to considering the reactions occurring in the flaming of cellulosic materials or the mechanisms by which that combustion may be prevented, it is desirable to review briefly the chemical nature of cellulose and its behavior under normal conditions.

It should be borne in mind that in considering the flameproofing of cotton textiles one is dealing with the chemical treatment of a very complex polymeric material. In order to properly interpret the behavior of flame-retardant materials and also the performance of flameproofed fabrics it is essential that one consider carefully the known reactions of cellulose under the influence of acids, bases and oxidizing materials. A clear understanding of the causes and mechanisms of the hydrolytic and oxidative degradations of cellulose will contribute considerably to an understanding of the changes observed in the course of thermal degradation. Furthermore, the performance of treated fabrics in the course of normal use and storage under various environmental conditions can be interpreted only on the basis of the known reactions of the cellulose molecule.

Accordingly, the following sections have as their purpose a thorough presentation of the basic structure, fundamental properties and known reactions of cellulose.

A. NATURE OF CELLULOSE

Henry A. Rutherford

1. OCCURRENCE AND STRUCTURE OF CELLULOSE

Of all the organic compounds which are found in nature, the material called cellulose is the most abundant. As the name implies, it is the chief constituent of the cells of plant tissues, and as a result it is widely distributed throughout the world. Not all naturally occurring cellulosic materials, however, are of the same content of cellulose. Some fibrous plant tissues, notably ramie and cotton, contain a high percentage of the material, while substances such as wood may contain as little as 40% of cellulose. The non-cellulosic constituents consist principally of lignins, pectins, fats and waxes.

The principal sources of the natural cellulosic textile fibers are the seed hairs and the bast fibers. The most important seed hair is cotton and among the bast fibers are flax, jute, hemp, and ramie. Differences in the nature and content of both the cellulosic and non-cellulosic constituent determine, to a large extent, the fiber chosen for a particular use. Thus cotton, which is fairly high in cellulose content and which is easily purified finds use in fabrics for clothing, while ramie, although it contains a high quality cellulose, is brittle, inelastic, and purified with great difficulty finds extremely limited use as a textile material. It is considered beyond the scope of this writing to delve further into the various sources, properties and uses of all the vegetable tissues which contain cellulose; a complete description of these aspects may be found elsewhere.¹

Because of its abundance and high degree of purity and the ease of removal of non-cellulosic substances therefrom, the cotton fiber has been the source of cellulose for most investigations dealing with the chemistry of this complex material. The experimental evidence at hand indicates that indeed there are no differences in chemical properties of purified cellulose from various sources, although there may be differences in rates of reactivity of the groupings brought about by certain dissimilarities in physical structure.

The native or raw cotton fiber consists of a primary and a secondary wall. The latter, which comprises the bulk of the fiber and the backbone of textiles made from cotton, consists practically entirely of cellulose. This secondary wall is enclosed by the thin so-called primary wall made up of fine criss-crossing strands of cellulose embedded in a membrane formed principally of wax and pectic substance, the latter combined with cations such as calcium, magnesium, sodium, potassium, iron, and aluminum. The lumen, or central canal, which is prominent in many fibers, also contains a small amount of these non-cellulosic constituents. The microscopic structure is revealed in Figures 1 and 2, which show cotton fibers in longitudinal and cross-sectional view, respectively.²

During manufacturing, more or less of the non-cellulosic materials may be removed from the raw fiber depending upon the severity of the process employed. In the preparation of a fabric such as heavy duck for tarpaulins or awnings, the cotton itself is subjected to no chemical processing whatsoever and the resulting product contains, for all practical purposes, raw cotton. On the other hand, fabrics for clothing, for reasons of ease of

¹ "Cellulose and Cellulose Derivatives," edited by Emil Ott. Interscience Publishers, Inc. (1943).

"Cellulose Chemistry," Emil Heuser. John Wiley & Sons, Inc. (1944).

"Introduction to the Chemistry of Cellulose," Marsh and Wood. Chapman & Hall, Ltd. (1942).

² Hock, C. W., Ramsay, R. C., and Harris, M., *J. Research Nat'l Bur. Standards*, 26, 93 (1941).

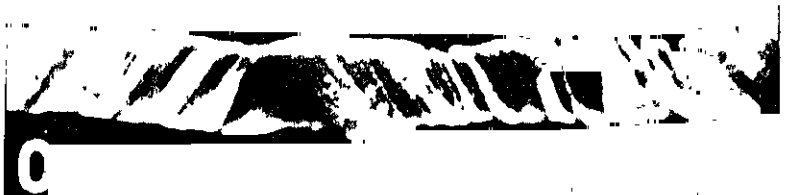
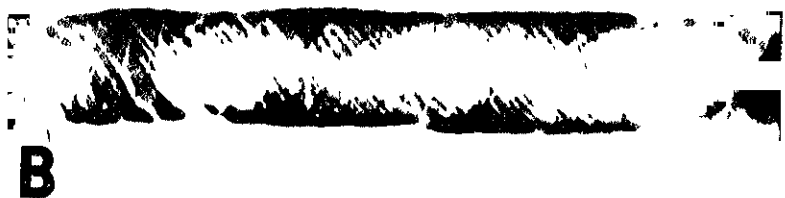
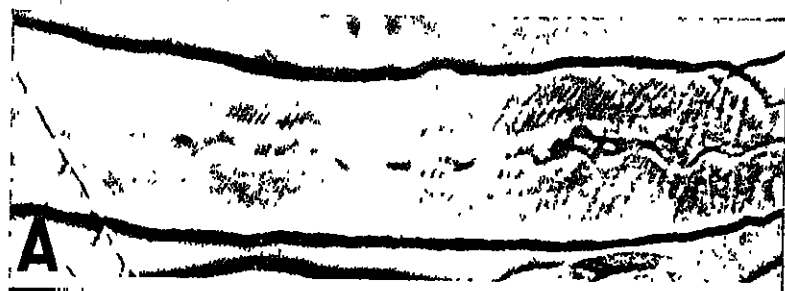


Figure 1 Mature fibers swollen to show the outer winding. A, photographed in ordinary light; B and C, between crossed nicols. C shows a reversal of the winding. Magnification $\times 420$ (Hock, Ramsay and Harris²)



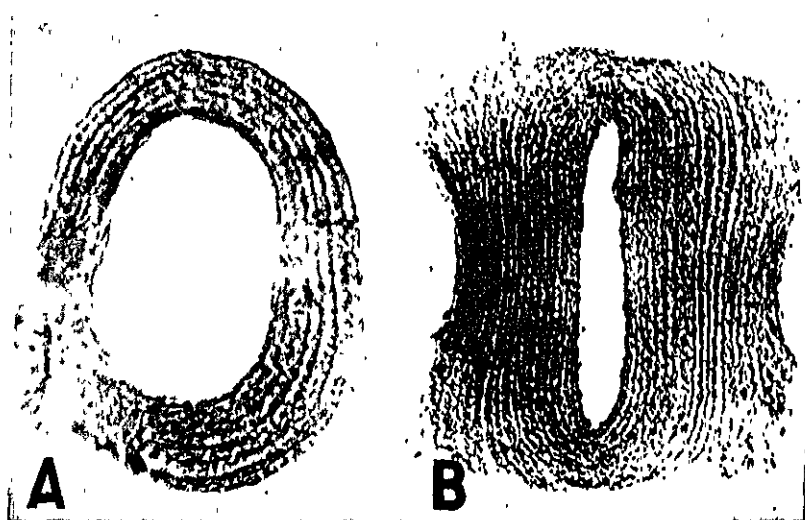
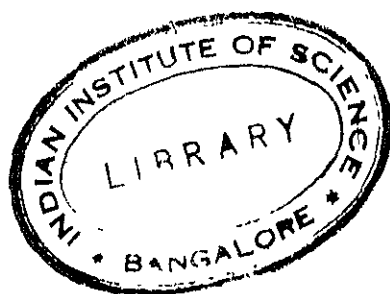
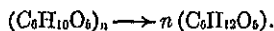


Figure 2. Cross section of cotton fibers swollen in dilute cuprammonium hydroxide solution to show "growth rings." A and B are 25-day and mature fibers, respectively. Magnification of A, $\times 925$; of B, $\times 400$. (Hock, Ramsey and Harris²)

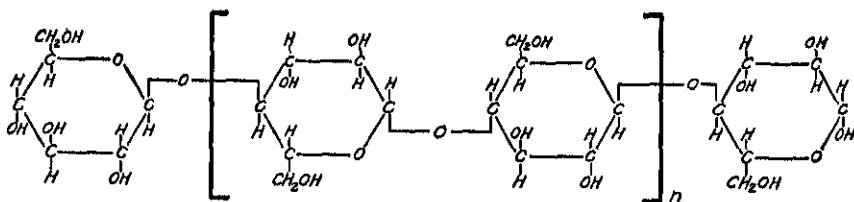


dyeing, fastness of color, etc., are thoroughly kier-boiled, bleached, soured and soaped, and the finished product is practically pure cellulose. The properties of either type of end product are, of course, intimately associated with the nature of the cellulose, and any changes in the latter brought about by one treatment or another are usually revealed in a change in properties of the fabric.

As early as 1842, it was recognized that cellulose was a constituent of wood, cotton lint, roots, and various other fibrous tissues, and that it was closely associated with the dextrorotatory sugar, glucose. Elementary analysis indicated the empirical formula $C_6H_{10}O_5$ and hydrolysis with mineral acid gave yields of glucose to the extent of at least 95% of the theoretical, assuming the conversion



Without going into the details and experimental proof of the structure of cellulose,⁸ it suffices to say that all evidence points to the formula



Molecular formula for cellulose

in which a large number of β -glucose units are joined together by means of oxygen bridges in the manner shown. These are referred to as 1, 4-glucosidic linkages, and arise by the elimination of the elements of water between the hemiacetal group on carbon atom 1 of one unit and the hydroxyl group on carbon 4 of the adjacent unit. The letter n denotes the number of anhydro-glucose residues which occur between the two ends of the cellulose chains. This number is by no means a fixed one and in the various types of native cellulose it ranges from averages of about 1500 to 3000. The total number of units in a cellulose chain is referred to as its degree of polymerization (D.P.). This number may be calculated by dividing the molecular weight by 162, the weight of an anhydro-glucose residue. The cotton fiber, or any cellulosic fiber, however, does not contain a single chain, but is a composite of many chains which are most probably of different lengths. It is therefore heterogeneous with respect to molecular size, or polymolecular. Thus, when reference is made to the degree of polymerization of a cellulosic material, the value represents

³ This may be found in review form in a paper by Freudenberg, K., and Blomquist, C., *Ber.*, 68B, 2070 (1935).

the average length of the many chain molecules of which it is comprised.

There are a number of methods available for the determination of the molecular weight of cellulosic materials. The classical ones used for low-molecular-weight organic compounds, however, cannot be applied and recourse is had principally to the viscosity, osmotic pressure, or end-group methods. The first of these, *i.e.*, the property of viscosity, is determined by the dissolution of the cellulose in a suitable solvent, usually cuprammonium hydroxide, followed by an ordinary viscometric measurement. The viscosity method is a relative rather than an absolute one and requires calibration. At the present time, the most reliable procedure for this purpose appears to be ultracentrifugal analysis. Thus, Kraemer⁴ showed that the weight-average molecular weight as determined by the ultracentrifuge was proportional to the intrinsic viscosity for cellulose and some of its derivatives, and derived constants which could be used for the calculation of molecular weight from viscosity. (Recent work by Gralen indicates that for cellulosic materials of very high molecular weight, a strict proportionality between intrinsic viscosity and molecular weight does not apply.) The osmotic pressure method at present is practical for use on derivatives of cellulose only. The end-group procedure involves the determination of the quantity of either the aldehyde groups which occur at one end of the cellulose chains, or the tetrahydroxy glucose residues which occur at the other (see formula, page 15).

Since each of the above properties, *i.e.*, viscosity, osmotic pressure, or end-group content is a function of the average molecular weight, these quantities are useful in determining the extent of degradation of cellulose brought about by various treatments. Each method, however, has certain limitations. These will be discussed as the occasion arises. For the most part, the viscosity of cellulose in cuprammonium has been the most practical method for the evaluation of molecular weight.

It is not surprising that rather wide variations in molecular weights of native celluloses have been found. In general, the highest values are obtained by ultra-centrifugal methods, and the lowest by end-group methods. A critical comparison of all the different procedures is not possible, however, since the methods have been applied to different products.

The manner in which the cellulose chains are arranged in a fibrous material, *i.e.*, the nature of the molecular structure, has been a matter of controversy for some time. Notable contributions in this respect have been made by Sponsler and Dore,⁵ Mark,⁶ and Meyer and Misch.⁷ The

⁴ Kraemer, E. O., *Ind. Eng. Chem.*, 30, 1200 (1938).

⁵ Sponsler, O. L., and Dore, W. H., Fourth Colloid Symposium Monograph, Chemical Catalog, New York (1926).

⁶ Mark, H., *J. Phys. Chem.*, 44, 779 (1940); Meyer, K. H., and Mark, H., *Ber.*, 61, 593 (1928); Kratky, O., and Mark, H., *Z. Phys. Chem.*, B36, 129 (1937).

⁷ Meyer, K. H., and Misch, L., *Helv. Chim. Acta*, 20, 232 (1937).

generally accepted picture at the present time is represented in Figure 3. It is seen that the fibrous structure is made up of molecular chains of various lengths lying roughly parallel to the fiber axis, and that in some regions they lie more closely together and possess a higher degree of order than in others. Regions of close lateral packing where the chains are parallel are designated as "crystalline," and these are differentiated from amorphous areas which possess a lesser degree of order. The former produce the characteristic x-ray diffraction pattern of cellulose, while the latter introduces the general fogging which is almost always in evidence. Although it is not possible to draw a sharp line of demarcation between these two phases because of the merging of one into the other (brought about by the continuity of the cellulose chains), the bulk of most natural cellulosic fibers is thought to be "crystalline." Attempts have been made

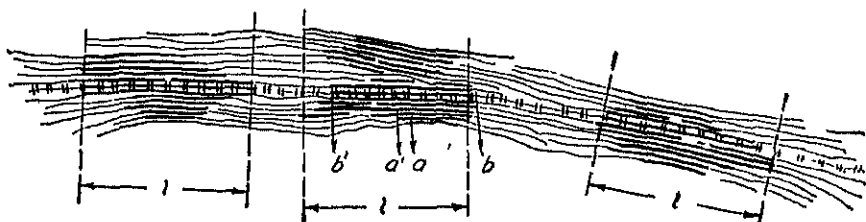


Figure 3. Schematic representation of cellulose crystallite structure showing how main valence chains pass through more than one micelle (fringe micellar theory). (Mark⁹)

a , a' , b' , molecular ends inside the crystallized region of one micelle, b , molecule end outside the crystallized region; l , length of crystallized region.

to estimate the proportion of each by methods which involve the ease of reactivity of various chemical agents with the fibrous material⁸ and, as might be expected, the values which have been obtained vary with the method employed.

Certain of the physical properties of fibers are believed to be related to the relative properties of crystalline and amorphous cellulose present. For example, the strength is contributed primarily by the more highly crystallized areas. The presence of a large proportion of the latter also leads to brittleness. On the other hand, there is ample evidence to indicate that the amorphous portions contribute principally to elasticity, and are involved in swelling, dyeing, and phenomena of a similar nature.⁹ These less highly organized areas presumably react more readily with most chemical agents, a property which has been used to estimate the quantity of easily accessible regions in various types of cellulosic materials. The resistance of

⁸ Nickerson, R. F., *Ind. Eng. Chem.*, **33**, 1022 (1941); Goldfinger, G., Mark, II., and Siggia, S., *Ind. Eng. Chem.*, **35**, 1083 (1943).

⁹ Mark, II., *J. Phys. Chem.*, **44**, 764 (1940).

highly ordered or crystalline spots to such a simple compound as hydrochloric acid has been demonstrated.¹⁰

It is rather obvious from Figure 3 that the length of the cellulose chains in a fiber will also have a profound effect on its strength, high strengths being associated with long chains. Thus, from a practical point of view, it is desirable during the processing of, for example, cotton materials to maintain as nearly as possible the original chain length of the cotton cellulose. In so doing, a fabric of high quality is attained.

2. CHEMICAL NATURE AND REACTIONS OF CELLULOSE

From a knowledge of the composition and structure of cellulose, it is readily seen that it is similar in nature to a polyhydric alcohol and to a polysaccharide. Its chemical reactions are therefore similar to that of simpler organic compounds of this type. It contains at one end of each cellulose chain a hemiacetal or potential aldehyde group, and at the other a hydroxyl group not present on the remaining anhydro-glucose residues. There is nothing unique about this hydroxyl group (which is in the 4 position), except that its presence makes possible the estimation of the average molecular weight through the determination of tetrahydroxy glucose. Two secondary hydroxyl groups are found in the 2 and 3 positions. The two may be considered as a single glycol group, and as will be seen later they sometimes react as one. Finally, each of the anhydro-glucose residues carries the primary alcoholic group characteristic of glucose.

The methods of analysis which are applicable to the simpler organic compounds are not always suitable for cellulose, primarily because of the lack of sufficient sensitivity. For example, the hemiacetal or potential aldehydic reducing group at one end of the cellulose chain might be expected to undergo reactions characteristic of this group. Indeed it does, but the number of these groups in, for example, several grams of cellulose is so small that their detection by ordinary methods is extremely difficult. Another difficulty arises from the fact that cellulose is insoluble, and the reactions must take place in a heterogeneous system.

With respect to the alcoholic nature of cellulose, most of the reactions involve the formation of derivatives, i.e., the adding-on to the chain molecule a group or groups to create certain characteristics not present in cellulose itself. Such processes are involved in the formation of alcoholate-like compounds, ethers (ethyl cellulose) and esters (cellulose acetate), all of which have wide commercial application.

Inorganic esters of cellulose such as cellulose nitrate, sulphate, and phosphate are well known and are not difficult to prepare. The first of these, however, is the only derivative of this type which at present has

¹⁰ Davidson, G. F., *J. Textile Inst.*, **34**, T87 (1943).

any commercial significance. The phosphate promises to assume some importance, particularly in the formation of flame-resistant cellulose. The preparation of any of these derivatives involves straightforward organic chemistry, except that conditions must be well controlled in order to minimize effects which tend to reduce the length of the chain molecules.

One of the oldest and most important commercial reactions of cellulose involves the formation of a complex with alkalis. In 1844, Mercer noted that the properties of cellulose became radically changed when it was treated with 12 to 18 per cent sodium hydroxide; and since then many researches have been conducted to elucidate the nature of the chemical reaction. In spite of this, controversy still exists as to whether a true alcoholate, cellulose-O-Na, is produced or whether the sodium hydroxide forms an addition complex of the type $(\text{cellulose-OH})_x \cdot (\text{NaOH})_y$. In any event, the formation of the so-called soda cellulose finds extensive commercial application since the compound serves as an intermediate in the preparation of many derivatives. An example may be cited in the preparation of ethyl cellulose: the raw material is first treated with aqueous alkali to form soda cellulose



and this is then reacted with, for example, ethyl chloride



to form ethyl cellulose. The reaction is not unlike the preparation of ethers from aliphatic alcohols. The production of viscose rayon also utilizes as the first step the formation of soda cellulose which is subsequently xanthated with carbon bisulphide and then regenerated. Although commercially the formation of ethers of cellulose utilize soda cellulose as an intermediate, the alcoholic hydroxyls will react directly with ethylene oxide, diazomethane, and with sodium metal in liquid ammonia.

With respect to the process of mercerization, which involves treatment for a very short period of time with about 18% sodium hydroxide, the principal effects on cotton are to swell the fibers longitudinally, shrink them laterally, and give them a greater absorption of water, dyes, etc., as well as in increased chemical reactivity. When the treatment is carried out under tension, the fibers also acquire a smooth lustrous surface and exhibit an increase in strength. The increase in absorptive power and reactivity is ascribed to the formation of amorphous areas in the cellulosic structure at the expense of the crystalline portions.

Unlike the reactions of cellulose with sodium hydroxide, the formation of other metal alcoholates have no commercial value. From an academic point of view, however, studies of the reactions of such compounds as thallous ethylate to form the thallium alcoholate of cellulose has been of use in elucidating the structural characteristics of cellulosic materials. By

a clever method of analysis, the area of the internal surface or the number of available surface hydroxyl groups may be determined.¹¹

Finally, the formation of cellulose complexes, which is in all probability associated with the alcoholic nature of cellulose, cannot be overlooked. Cuprammonium hydroxide solutions are the best known solvents for cellulose, and the complex which is formed not only finds an academic use in evaluating molecular size, but serves as an intermediate in the preparation of cuprammonium or Bemberg rayon. Certain other organic bases such as dibenzyl-dimethylammonium hydroxide are excellent swelling agents and fair solvents for cellulose. Compounds of the tetraalkylammonium type have a potential value in that they dissolve cellulose and permit the preparation of derivatives in a homogeneous medium instead of a heterogeneous one, as in the case of the inorganic bases.

The alcoholic groups also enter into reactions which are sometimes detrimental to cellulosic materials. These involve oxidation of either or both the secondary and primary alcohol groups to aldehyde or carboxyl groups. A detailed discussion of degradation by oxidation follows in Section B.

The reactions characteristic of polysaccharides invariably involve a shortening of the cellulose chains, *i.e.*, hydrolysis of glucosidic linkages by the addition of water. This effect may be brought about directly by the use of acids, or it may result as a secondary process from activation of the glucosidic bond through oxidation of one or more of the hydroxyl groups. The intermediates between high molecular weight cellulose and glucose which are formed by this process also possess the properties of polysaccharides. That is to say, cleavage of the oxygen bridges between glucose residues lowers the chain length, but does not essentially alter the chemical properties.

B. NORMAL DEGRADATION REACTIONS¹²

Henry A. Rutherford

Cellulosic substances are readily degraded by acids, oxidizing agents, enzymes, heat, and light. With rare exceptions, the processes of breakdown are complicated and the chemical mechanisms of the reactions are not completely understood. This is particularly true of attack by enzymes, heat, and light, and it is not surprising when the chemical nature and structure of cellulose are considered. Not only are there a number of vulnerable points in the molecule, but the accessibility of these points is

¹¹ Harris, C. A., and Purves, C. B., *Paper Trade J.*, 110, 20 (1940).

¹² For a more comprehensive treatment of the degradation reactions of cellulose, see the author's sections in "Cellulose and Cellulose Derivatives," edited by Emil Ott, Interscience Publishers, Inc., New York (1943).

limited by the physical arrangement of the groupings and by the insolubility of the cellulosic material. Thus, it is expected that most chemical reactions would follow a heterogeneous course. Because of this, it has not been possible to develop with any degree of certainty the theoretical aspects of cellulose degradation. Theoretical considerations have been presented in recent literature principally by Mark, Meyer, Freudenberg, Kuhn, and Simha,¹³ but no conclusive experimental evidence is yet available to support the relations in a quantitative way. It is the purpose of this section to describe only those chemical degradation reactions of cellulose which are understood best, and to review briefly the properties of celluloses modified by various chemical means.

1. HYDROLYSIS OF CELLULOSE

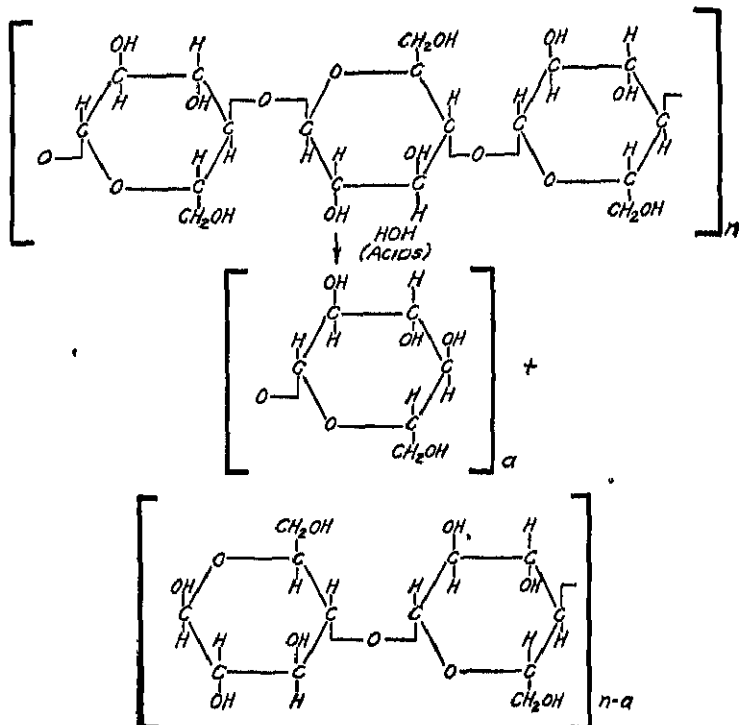
When a cellulosic material is subjected to the action of an acid, particularly one of the mineral acid series, a hydrolytic type of breakdown which involves a simple cleavage of 1, 4-glucosidic linkages occurs. The result of such an action is a shortening of the cellulose chain to produce fragments having lower average molecular weights than that of the untreated cellulose. The reaction is essentially a reversal of the procedure by which the chains are built up, and may be represented by the scheme given on page 22.

If the reaction is allowed to proceed far enough, glucose and a small amount of its acid decomposition products are the final substances obtained. For the reasons mentioned above, the degradation does not take place in a uniform manner and if the reaction is stopped prior to completion, the partially hydrolyzed cellulose may be divided into a number of fractions, the molecular weights of which may vary between that of glucose and the original material itself. Thus, the degradation product consists of a homologous series of celluloses in which the macromolecules may have arrangements similar to those in the original material, but are non-homogeneous in character and exhibit lower average molecular chain lengths than the original cellulose. This mixture of cellulosic substances obtained by the action of acids is referred to by the generic term "hydrocellulose." Hydrocellulose is thus not a homogeneous chemical entity, as earlier investigators believed.

Girard¹⁴ was one of the earliest investigators to find that hydrocellulose could be prepared by a number of methods. He was able to produce a series of white, friable powders by immersion of cellulose in mineral acids,

¹³ Meyer, K. H., Hopff, H., and Mark, H., *Ber.*, **62B**, 1103 (1929); Montroll, E. W., and Simha, R., *J. Chem. Phys.*, **8**, 721 (1940); Simha, R., *J. Applied Phys.*, **12**, 569 (1941).

¹⁴ Girard, A., *Compt. rend.*, **81**, 1105 (1875); **88**, 1322 (1879); *Ann. Chim. Phys.*, **24**, 337 (1881).



Molecular reaction showing the hydrolytic breakdown of cellulose in the presence of an acid.

by the action of moist gaseous halogen acids, or by impregnating the fiber with solutions of certain organic acids and then heating the materials a 100°C . The organic acids are found to produce tendering at a slower rate than the mineral acids. This appears to be related to the fact that the former are weaker acids.

Birtwell, Clibbens and Geake¹⁵ were the first to make a thorough study of the factors which influence the rate of hydrolysis of cellulose by acids. Primarily, the rate is a function of the kind of acid, its concentration, and the temperature. By the proper control of each condition, it is possible to duplicate with a fair degree of precision the preparation of a hydrocellulose of given physical and chemical properties.

Two of the most characteristic changes which accompany the degradation by acids are a decrease in viscosity and in strength of the cellulose. As stated in Section A above, both of these properties are dependent to a considerable extent upon the average length of the cellulose chain molecules, and it is not surprising that a definite and practically constant relation between loss in strength and decrease in viscosity is found. This rela-

¹⁵ Birtwell, C., Clibbens, D. A., and Geake, A., *J. Textile Inst.*, 17, T145 (1926).

tionship, expressed in terms of the reciprocal of viscosity, namely, the fluidity,¹⁶ is emphasized in Figure 4. The unique feature of this relationship is that it is independent of the nature and conditions of the acid treatment, and it obtains for a pure cellulosic fiber, yarn, or fabric. Results of this kind lead to the conclusion that the degradation of cellulose by acids during the early stages of attack is fairly uniform over the chain molecules, and that the glucosidic linkages are broken more or less at random. Highly localized attack on cellulosic fibers could result in a large

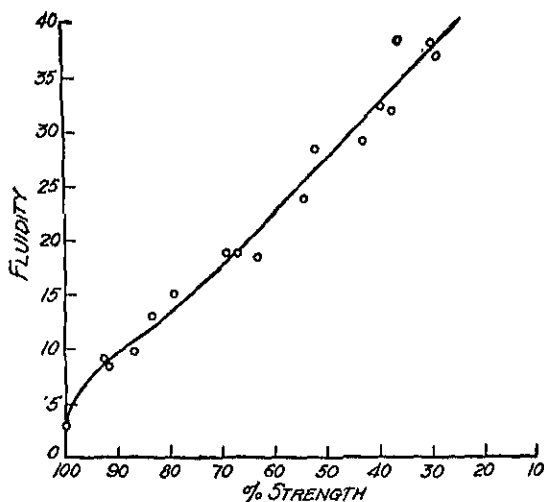


Figure 4. The relation between breaking strength and fluidity of hydrocelluloses. (Clibbens and Ridge¹⁷)

loss of strength without an accompanying appreciable increase in fluidity.

- Although from a practical point of view, the most important aspects of cellulose degradation are in the early stages of attack, a number of investigations have been directed toward an examination of the properties of cellulose after prolonged treatment with acidic substances. In a heterogeneous system, it is invariably found that the rate of reaction as shown by the properties of, *e.g.*, strength and fluidity, takes place rapidly at first (*i.e.*, during the early stages) and slows down considerably as the duration of treatment is prolonged. It is of interest that, judged by some properties of the residual cellulose, the hydrolysis appears to stop short of completion. Thus, for example, the fluidity of cotton cellulose in cuprammonium reaches a maximum of about 50 upon treatment with hydrochloric or sulphuric acid instead of the maximum value possible, about 63. This

¹⁶ As a matter of convenience in referring to viscosity characteristics, the term "fluidity," which is the reciprocal of viscosity, was introduced. The use of this term is commonly employed in the description of textile materials.

¹⁷ Clibbens, D. A., and Ridge, B. P., *J. Textile Inst.*, 19, T389 (1928).

is shown by the results obtained by Davidson¹⁰ (Figure 5). When mercerized cotton was treated in a similar manner, a maximum fluidity about 60 was attained. The degrees of polymerization calculated from Kraemer's constants, which correspond to fluidities of 50 and 60, respectively, are 190 and 95. Thus, the degradation is far short of being complete, particularly in the unmercerized cotton. These results, in addition to the observation that the x-ray diagram of the powdery residue was identical with the original cellulose, indicate that the acid does not penetrate the crystalline portions of the fibers and that the action is confined to hydrolysis of glucosidic linkages situated in the amorphous

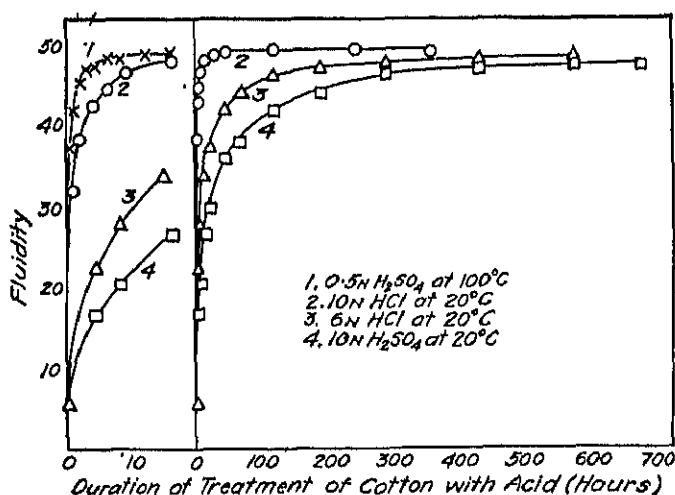


Figure 5. The effect of inorganic acids upon fluidity, showing both the extent and relative rates of attack. (Davidson¹⁰)

regions. It is generally assumed that mercerization increases the content of amorphous areas in cotton, and the higher rate of hydrolysis found with the mercerized as compared with the unmercerized supports this view.

Although other properties such as solubility in alkali and moisture absorption also reach an approximately constant value after prolonged hydrolysis, it should be emphasized that the action does not entirely cease, but continues extremely slowly. Ultimately, even in a heterogeneous system, the cellulose is completely destroyed.

A more complete study of the relation between strength and degree of polymerization of cellulose degraded by acids was made by Staudinger and Sorkin.¹⁸ It was found that materials having D.P.'s of 200 to 250 disintegrated on handling, while in the range of 250 to 700 both the breaking strength and the elongation at the break increased with increase in D.P.

¹⁸ Staudinger, H., and Sorkin, M., *Ber.*, 70B, 1505 (1937).

Further increases beyond 700 resulted in only slight further improvement in these properties.

An obvious result of the shortening of the cellulose chains in the manner indicated above is a production of new aldehydic end groups. Accordingly, another characteristic change which accompanies the formation of hydrocellulose is an increase in reducing properties. The presence of these groups is shown by the reducing action of hydrocellulose on copper (*e.g.*, Fehling's solution), ammoniacal silver nitrate, and by reaction with phenylhydrazine, hydroxylamine, Schiff's reagent and ethyl mercaptan. The most commonly used method for determining this type of end group has been the well-known "copper number" method developed originally by Schwalbe.¹⁰ The method depends on the reduction of copper from the cupric to the cuprous state by the cellulosic material. The original procedure has been frequently modified, but, despite numerous improvements, it still leaves much to be desired. Thus, the copper number obtained for a particular sample has been shown to depend on such factors as temperature of heating, time of heating, ratio of weight of sample to weight of solution, physical state of the sample (fineness of cutting or grinding), composition of the solution containing the cupric ion, solubility of the Cu_2O formed in the mother liquor, and the progressive degradation of the cellulose by the alkaline solutions employed. For these reasons, the copper number at best can be considered to be only a rough measure of the content of reducing groups of a cellulosic material. The results obtained by this method, however, have more significance when it is applied to a homologous series of samples prepared by similar treatments. Thus, some interesting relationships are obtained between copper number and *e.g.*, viscosity of hydrocelluloses. It has been shown that when the copper number lies within the limits of 0.3 and 4.0, its relationship to viscosity can be expressed by the equation $N_{\text{Cu}} V^2 = 2.6$ where N_{Cu} is the copper number and V is the log of the relative viscosity.

The validity of the chemical mechanism of hydrocellulose formation is further demonstrated by the direct relation between aldehydic reducing groups, determined by a method specific for these groups, and fluidity. The relationship for a series of hydrocelluloses down to molecular chain lengths which correspond to almost total loss in strength of cotton fibers is shown in Figure 6.

The decrease in molecular size of cellulose during degradation with acids is also accompanied by an increase in solubility, especially in alkaline solutions. However, even boiling water dissolves a fraction of hydrocellulose which is higher in reducing power than the original hydrocellulose. When hot dilute solutions of alkalis are used, additional soluble decomposition products are obtained. The loss in weight, the effect on

¹⁰ Schwalbe, C. G., *Ber.*, **40**, 1347 (1907).

fluidity and breaking strength, and the change in copper number of hydrocelluloses on boiling in alkaline solutions has been rather extensively investigated. In general, it has been found that the reducing power of the hydrocellulose on treatment with hot alkali is decreased and may even fall to nearly zero without necessarily being accompanied by extensive weight losses. The solubilities in alkali of hydrocelluloses appear to be related to the reducing power of the material; that is, hydrocelluloses of the same copper number have been shown to have the same solubility. On boiling in alkaline solutions, they sometimes exhibit a considerable loss in weight without undergoing a large change in fluidity, and in this respect they differ from most other types of modified celluloses.

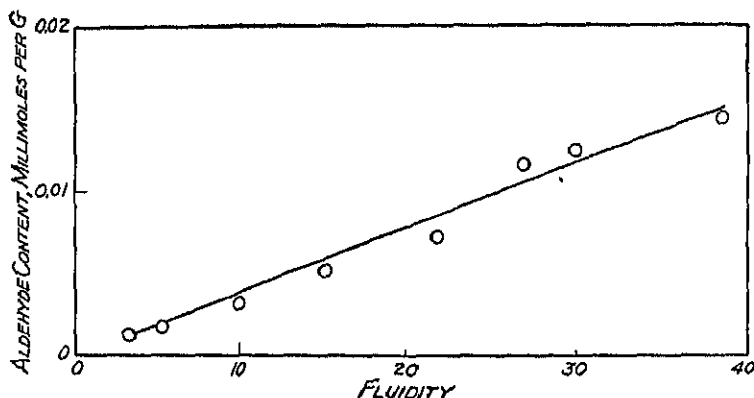


Figure 6. Relation of aldehydic content of hydrocelluloses to fluidity.
(Martin, Smith, Whistler, Harris²⁰)

The practical aspects of degradation of cellulose by hydrolysis were brought out a number of times during World War II. It was perhaps emphasized more during this period because of the many treatments which were developed to give cotton fabrics certain desirable characteristics or to prolong their useful service life. One such treatment was employed in the production of the so-called Duck, Cotton; Fire, Water, Weather, and Mildew Resistant. Studies of the mechanism of deterioration of this type of fabric revealed that in many instances the chlorinated paraffin present in the finish was unstable to heat and/or light, and liberated hydrogen chloride. In the presence of moisture, this compound had an adverse effect on the cotton, the severity of attack depending upon the conditions which prevailed at the point of usage. An examination of the strength-fluidity

²⁰ Martin, A. R., Smith, L., Whistler, R. J., and Harris, M., *J. Research Nat'l. Bur. Standards*, 27, 449 (1941); *Am. Dyestuff Repr.*, 30, 628 (1941).

relationships of damaged tentage sometimes gave results which were similar to the relation shown in Figure 4 for hydrocelluloses. (This was regarded as strong evidence that the breakdown was caused by hydrolysis of the cellulose and not by some other means. (See Chapter VII, Section A, 2-b.) This knowledge lent a scientific background for the incorporation of basic substances in the finish for the purpose of absorbing HCl, thus preventing the attack on the cotton. Experience with this fabric has shown that the durability was greatly improved after the use of basic substances by the finishers became widespread.

In view of the well-known sensitivity of cellulose to acids, it is safe to say that any flameproofing treatment for cotton textiles should not leave an excessive acidic residue on the fabric. Some rather extensive studies have been carried out to reveal the level of acidity at which cotton begins to deteriorate rapidly. Obviously, there is no definite answer to this question because of the dependence of rate of breakdown on the severity of other conditions (*e.g.*, temperature). However, it appears that fabrics which are to be subjected to outdoor weathering or to elevated temperatures indoors should not give water extracts which are below pH 6.0.

2. OXIDATION OF CELLULOSE

In contrast to hydrolysis, the oxidation of cellulose is an extremely complicated process, and results in the formation of a wide variety of modified celluloses, the structures of which are not known in the majority of cases. The reaction products are, in general, heterogeneous with respect to both structure and molecular size and do not constitute chemical entities. For this reason the term "oxycellulose" has no meaning other than to identify a cellulosic material which has been attacked by an oxidizing agent. The need for more specific terms to identify the products has been recognized, and there are indications that a system of nomenclature is forthcoming. To avoid confusion, however, the present discussion will follow the conventional methods of designating the products of oxidation.

From a technical point of view, the oxidation of cellulose is a subject of great importance. In the commercial processing of cellulose, for example, bleaching treatments are frequently required to remove the colored substances which impart a yellowish tint to the material; in such treatments, oxidizing agents such as hypochlorite or hydrogen peroxide may be employed, and unless care and control are exercised, severe tendering of the cotton cellulose, due to oxidative degradation, may occur. Cellulose is also readily degraded by oxygen in strongly alkaline solutions, a reaction which is utilized in the preparation of viscose rayon.

The properties of any oxycellulose depend upon the method by which it is prepared, but in general it may be said that in neutral or acidic solu-

tions, oxycelluloses of the *reducing* type are formed (i.e., they show high content of reducing groups as measured by the copper number method), whereas in alkaline solutions, the *acidic* type of oxycellulose is formed. The latter has sometimes been referred to as the "methylene type" since it exhibits rather high affinity for methylene blue. Acidic celluloses tend to show high retention of alkali presumably due to the presence of carboxylic acid groups.

The manner in which hydrogen-ion concentration may influence the rate or type of oxidation has been extensively studied by many investigators. Oxidation generally proceeds most rapidly near pH 7 for this reason neutrality is always avoided in the commercial bleaching of cotton. This is shown for oxidation by chlorine solutions in Figures 7 and 8. The data also emphasize the fact that the rate or extent of oxidation is not necessarily ascertained by the measurement of the change in any one given property such as copper number or methylene blue absorption; thus, as indicated by the copper number method, the rate is greater at pH 4.6 than at pH 11.2, whereas, as indicated by methylene blue absorption, the effects of pH appear to be reversed.

The rate of oxycellulose formation is also influenced by temperature, concentration of oxidant, and the nature of the oxidizing reagent. As an example of the last, hypobromite is much more effective for a given set of conditions than hypochlorite. Finally, the rate of oxidation of cellulose may be greatly accelerated by the presence of another oxidizing substance in the system. Thus, oxidation with dichromate in the presence of oxalic acid is far more rapid than in the presence of sulfuric acid. In another example, it has been shown that when cotton, on which a red vat dye has been absorbed, is treated with hypochlorite, the oxidation of the cellulose is greatly accelerated.

The extensive literature on oxycellulose is indicative of the enormous amount of work which has been done in this field and yet, at the present time, it must be concluded that the chemical mechanism of oxidative attack by most reagents is not clearly understood. It would appear that attack on cellulose would be confined to three points in the anhydroglucose residue of the cellulose chain: (1) The aldehydic end groups, of which there are few if any in native cellulose, could be oxidized to carboxylic groups. Such a process would not be expected to result in significant changes in the properties of celluloses of high average chain lengths, but might alter considerably the properties of an appreciably degraded hydroxymethyl cellulose. (2) The primary alcohol groups could be oxidized to the aldehyde or carboxylic acid depending upon the oxidizing conditions. Such oxidations would lead to a reducing type or an acidic type of oxycellulose depending upon whether the reaction proceeded to the aldehyde or to the acid. (3) The glycol group (the 2,3-dihydroxy group) of the glucose residue could be oxidized with the formation of ketonic, aldehydic, or carboxylic groups.

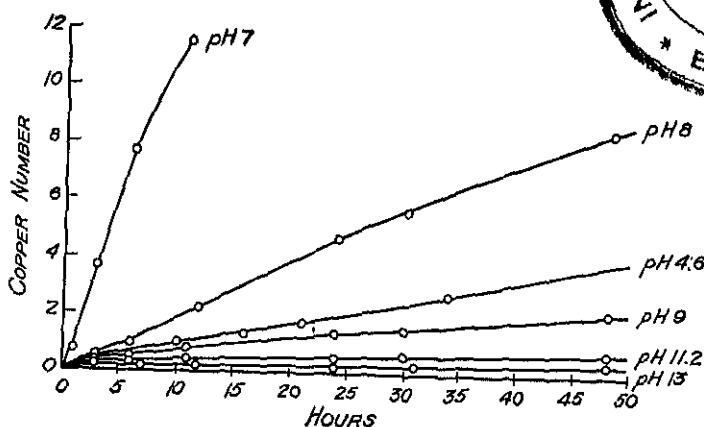
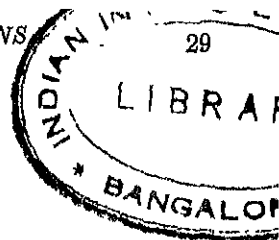


Figure 7. The effect of pH on the rate of increase of copper number. (Clibbens and Ridge²¹)

0.04 N sodium hypochlorite at 25° C.; ratio of cotton to solution 1:100.

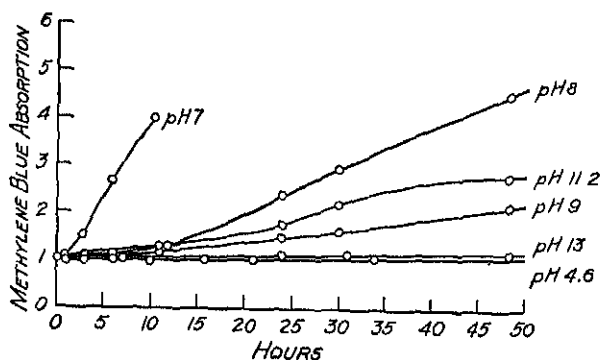


Figure 8 The effect of pH on the rate of increase of methylene blue absorption (Clibbens and Ridge²¹)

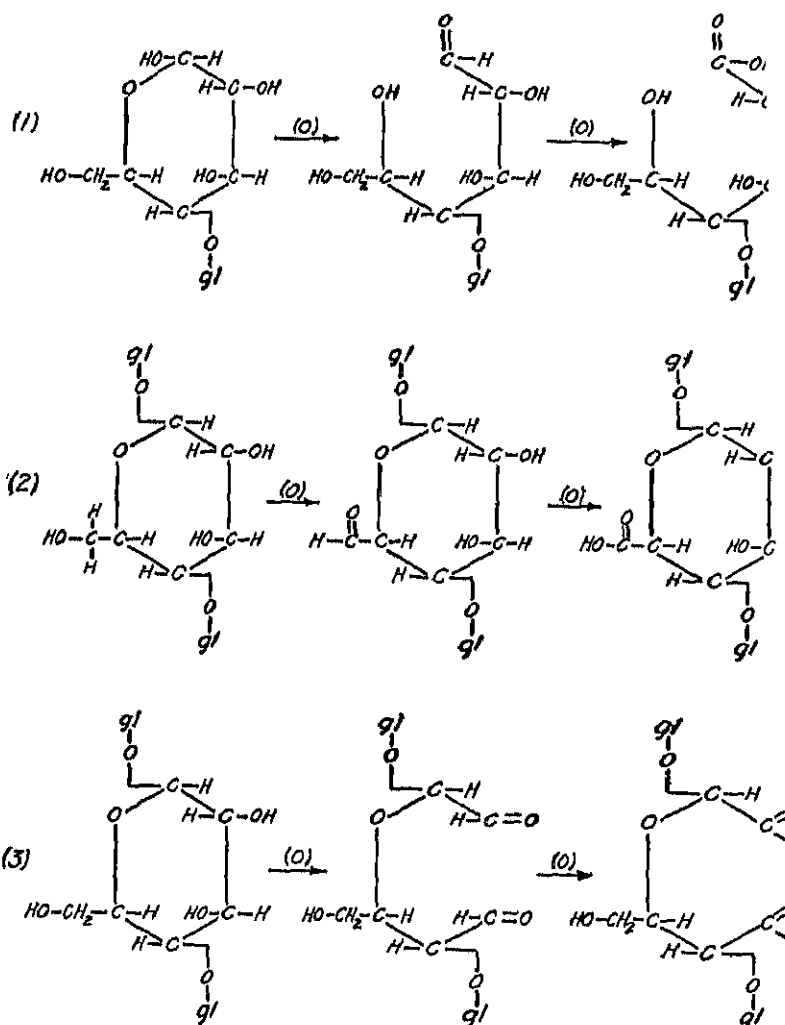
0.4 N sodium hypochlorite at 25° C.; ratio of cotton to solution 1:100.

²¹ Clibbens, D. A., and Ridge, B. P., *J. Textile Inst.*, 18, T135 (1927).

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boxylic groups, depending upon the course of the reaction. These reactions may be represented by the following formulae:



Molecular reactions showing the oxidation of cellulose at

- (1) the aldehydic end group;
- (2) the primary alcohol group;
- (3) the glycol group.

A major difficulty in most attempts to ascertain the course of the oxidation of cellulose has been the lack of analytical methods of sufficient specificity and sensitivity to determine accurately the number of any of the above-mentioned groups which might be formed, or to allocate them to their positions in the glucose residues. The limitations of such methods as those involving the measurement of copper number as an estimate

reducing groups or methylene blue absorption as an estimate of acidic groups are well recognized, and quantitative conclusions based on their use may be open to criticism. Nevertheless, considerable use has been made of them and they have been helpful in obtaining a rough qualitative picture of the course of some of the reactions. More recently, a number of new methods for the estimation of aldehydic and carboxylic groups in cellulose have been developed and are at present being applied to quantitative studies of the functional groups in various types of oxycelluloses.

Until recently, it was widely assumed that the oxidative attack occurred at the primary alcohol groups in the cellulose chain molecules causing either weakening or actual scission of the glucosidic linkages. In favor of this assumption was the fact that many of the oxycelluloses yielded carbon dioxide during boiling with hydrochloric acid, a reaction which is characteristic of uronic acids. Oxidation of the primary alcohol group to the carboxyl group stage would result in the formation of a glucuronic acid anhydride residue. Unfortunately, the hypothesis of simple oxidation of the primary alcohol group to one of a carboxylic acid type does not adequately explain the behaviors of all of the various types of oxycelluloses. Thus, Clibbens and Ridge²² have shown that, whereas there is a proportional increase in cuprammonium fluidity and in copper number with decrease in tensile strength for hydrocelluloses, regardless of the type of acid used in their preparation, this proportionality does not exist for all types of oxycellulose. The data in Table 1 illustrate this point. Similarly,

Table 1. Relation Between Cuprammonium Fluidity and Strength of Hydrocellulose and Different Types of Oxycelluloses (Clibbens and Ridge)²²

Cuprammonium Fluidity	Percentage loss of strength (single-thread breaking load)			
	Caused by Acid Attack	Caused by Attack with Hypochlorite or Hypobromite	Caused by Attack with Dichromate plus H ₂ SO ₄	Caused by Attack with Dichromate plus Oxalic Acid
10	10	7	2	1
20	34	25	11	6
30	58	47	26	16

no relationship exists between copper number and tensile strengths for all types of oxycellulose. For example, a rise of one unit in copper number may correspond to complete loss in strength as in the case of alkaline hypochlorite modification, to 50% loss as in tendering by acids, or to practically no loss in strength as in the oxidation with dichromate. Since, on the basis of the molecular chain theory, both the fluidity and the tensile strength of cellulose are regarded as functions of chain length, this apparent anomaly was at first disturbing.

As a solution of this difficulty, Davidson²³ suggested that some types of oxidation do not result in direct scission of the chain molecules but reduce the chemical stability of some of the linkages in the cellulose chain

²² Clibbens, D. A., and Ridge, B. P., *J. Textile Inst.*, **19**, T339 (1928).

²³ Davidson, G. F., *J. Textile Inst.*, **29**, T195 (1938).

toward alkalis. This suggestion was based on the discovery of Cl and Ridge that the changes in fluidity and strength after boiling oxylloses in alkaline solutions were such that the fluidity-strength relationship was the same for all types of oxycellulose. Types of oxidation which rupture the chain would not have an appreciable effect on strength. At the same time, these types of modification result in a material which is more labile toward alkali and accordingly the fluidity in cuprammonium solution will be high. This, then, would explain the apparent lack of correlation between strength and fluidity for all types of oxycelluloses.

On the basis of this reasoning, Davidson further postulated that the fluidity of this type of oxycellulose could be determined without the use of alkaline solutions, then it would be possible to obtain a true measure

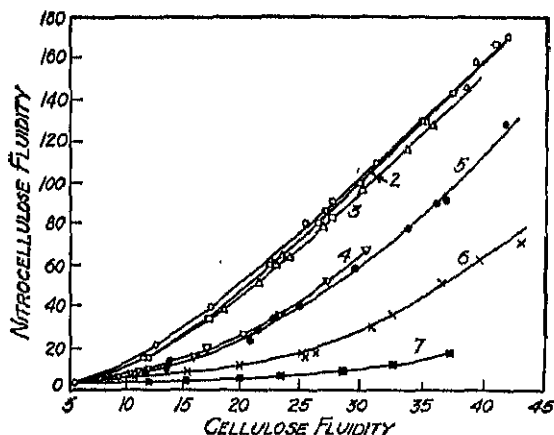


Figure 9. Relation between nitrocellulose fluidity and cuprammonium fluidity of modified cottons. (Davidson²⁸)

- | | |
|---------------------------|--------------------------------|
| 1. Hydrochloric acid. | 5. Neutral hypochlorite. |
| 2. Alkaline hypobromite. | 6. Dichromate + sulfuric acid. |
| 3. Alkaline hypochlorite. | 7. Dichromate + oxalic acid. |
| 4. Acid hypochlorite. | |

of the average length of the molecular chains as they exist in the cellulose. Fortunately, it was found possible to do this by first nitrating the celluloses and then determining the fluidity of the derived nitrocelluloses in acetone or butyl acetate solution. By this procedure, it was found that the discrepancies between strength and fluidity (i.e., oxycelluloses which exhibit high strength and high cuprammonium fluidity) disappeared. The oxycelluloses of the type characterized by high strengths also showed high nitrocellulose fluidities.

From the foregoing, it is readily seen why the relationship of cuprammonium fluidity to nitrocellulose fluidity as found for all types of hydrocelluloses does not exist for all types of oxycelluloses (Figure 9). If, however,

oxycelluloses are first boiled in alkaline solution, in order to complete the scission of the cellulose chains at or near the alkali-labile linkages, the nitrocellulose and cuprammonium fluidities change to a greater or less extent depending on the type of oxidative modification, and the relation

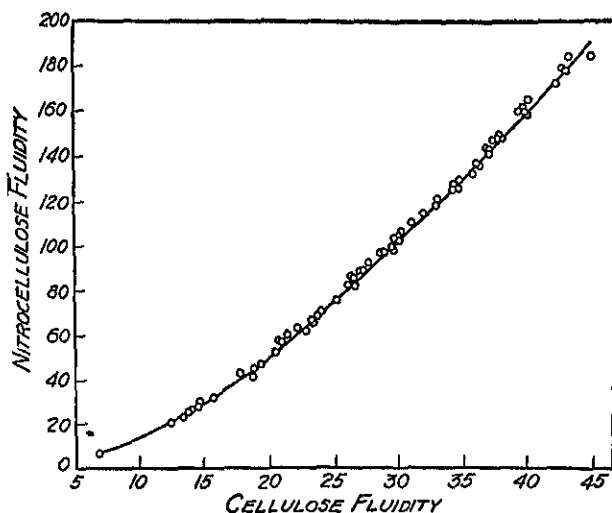
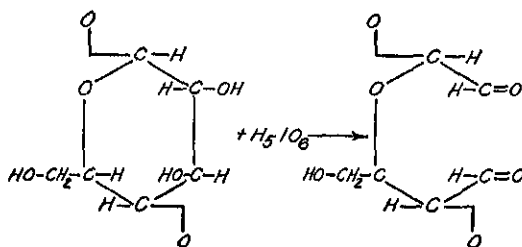


Figure 10 Relation between nitrocellulose fluidity and cuprammonium fluidity of modified cottons after boiling with sodium hydroxide solution. (Davidson ²⁸)

between the two fluidities can then be expressed by a single curve as shown in Figure 10. These experiments left little doubt that the reducing types of oxycellulose do contain alkali-sensitive linkages.

Davidson's hypothesis received considerable support from the investiga-

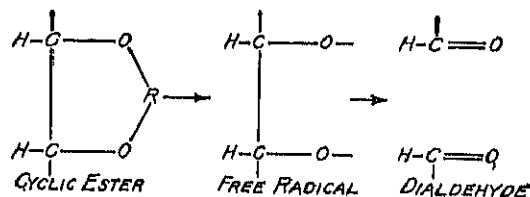


Molecular reaction showing the oxidation of cellulose by periodic acid.

tions of Jackson and Hudson who showed that in the oxidation of cellulose by periodic acid, cleavage of the glucose ring of the cellulose chain between carbon atoms 2 and 3 occurred with the conversion of the secondary alcoholic groups to aldehydes, according to the scheme above.

Subsequent to the work of Jackson and Hudson, the oxidation of cellulose by periodic acid has been studied extensively by Davidson,²⁴ and more recently by Rutherford, Minor, Martin and Harris,²⁵ and by Purves and coworkers.^{26,27} By carefully controlling the conditions, it is possible to confine the reaction to the oxidation of the secondary hydroxyl groups to aldehyde groups in accordance with the above equation. Thus, it can be shown quantitatively that two moles of aldehyde groups are produced for each mole of oxidant consumed. Further, the reducing groups of the periodic acid oxycelluloses can be converted to carboxyl groups, the direct titration of which provides an independent check on the content of the former.²⁶

The theoretical consideration of this type of oxidation reaction has led to some interesting results, and has enabled a prediction of the types of oxidizing agents which would effect a similar dialdehyde cleavage of cellulose.²⁷ Briefly, the requirements of the oxidant are as follows: (1) The central atom of the oxidant must have a diameter of about 2.5 to 3.0 Å, which is large enough to bridge the space between the hydroxyl groups in a 1,2 glycol (in the case of cellulose, the hydroxyl groups in the 2 and 3 positions). It must also be able to coordinate at least two hydroxyl groups in addition to the groups already attached to it. This enables the formation of an intermediate cyclic ester, as shown below, where *R* contains the central atom:



Molecular reaction showing oxidation of cellulose glycol group through the stages of cyclic ester, free radical, dialdehyde.

(2) The valence of the central atom must exceed by two units the valence of the next lowest stable state, and the oxidant should have a standard E_0 oxidation potential of about -1.7 volts with respect to the next lowest stable state. With these provisions, the valence of the central atom is reduced to form a free radical which rearranges to produce the dialdehyde as shown above.

²⁴ Davidson, G. F., *J. Textile Institute*, 31, T81 (1940); 32, T109 (1941).

²⁵ Rutherford, H. A., Minor, F. W., Martin, A. R., and Harris, M., *J. Research Natl. Bur. Standards*, 29, 131 (1942).

²⁶ Heidt, L. J., Gladding, E. K., and Purves, C. B., *Paper Trade J.*, 121, 81 (1945).

²⁷ Grangaard, D. H., Gladding, E. K., and Purves, C. B., *Paper Trade J.*, 115, 41 (1942).

It is of interest that common oxidants such as nitric acid, hypochlorite, dichromate, and permanganate do not have all the properties regarded as necessary for the dialdehyde type of oxidation and these are not known to oxidize cellulose in this manner. In fact, certain properties of celluloses modified by these agents make it clear that the mechanism does not follow that of periodic acid. In addition, oxycelluloses, which on the basis of certain criteria are of the same type, have been found to yield products which vary considerably in other properties. Thus, Davidson²⁸ has recently compared the properties of oxycellulose prepared with chromic acid and periodic acid and has observed rather profound differences in their behavior, although both reagents give reducing oxycelluloses as determined by the copper number method. He suggests that the cellulose is more uniformly attacked by the latter reagent, whereas the action of chromic acid is limited primarily to the noncrystalline regions. Supporting this suggestion is the fact that the x-ray patterns are not destroyed by a high degree of oxidation with chromic acid, whereas periodate gradually destroys the characteristic x-ray diagram of cellulose.

A different explanation for the behavior of chromic acid toward cellulose has been put forth by Staudinger and Sohn, who suggest that glucosidic linkages are converted to carbonic ester linkages, such linkages accounting for the alkali-lability of oxycellulose. However, as already pointed out by Davidson, a similar reason could be given to explain the mechanism of oxidation by periodic acid, which produces oxycelluloses that are even more alkali-labile than chromic acid oxycelluloses.

Another mechanism of oxycellulose formation which has been advanced involves as a primary reaction the splitting of 1,4-glucosidic linkages. This cannot be considered to be a general reaction since oxidations can occur under conditions which do not produce significant changes in chain length.

A very different type of oxidation has recently been described by Kenyon and his coworkers²⁹ who used nitrogen dioxide as the oxidizing agent. In contrast with most types of oxidations, which when carried to excess result in complete disintegration of cellulose fibers, it was found that at any stage of oxidation with nitrogen dioxide, the cellulose still retains its fibrous structure. Of especial interest, however, is the fact that the oxidation appears to be confined entirely to the primary alcoholic groups and results in the conversion of these groups to carboxylic acid groups. Oxycelluloses having carboxyl contents which approached theoretical values calculated on the assumption that all primary alcoholic groups have been oxidized were prepared by these investigators.

The effects of another gaseous oxidizing agent, ozone, have been in-

²⁸ Davidson, G. F., *J. Textile Inst.*, **32**, T109 (1941).

²⁹ Yackel, E. C., and Kenyon, W. O., *J. Am. Chem. Soc.*, **64**, 121 (1942).
Unruh, C. C., and Kenyon, W. O., *ibid.*, 127.

vestigated. It was found that, in the presence of water, the reducing type of oxycellulose is the principal product, although a slight increase in methylene blue absorption occurs. This is attributed, as in the case of other oxidizing substances, to the formation of some carboxyl groups. The rate of oxycellulose formation by ozone is greatly inhibited by first acetylating the cellulose, while the effect of mercerization is the reverse; that is, oxycellulose formation is accelerated by pretreatment with alkali.

A number of oxidizing agents such as hydrogen peroxide and sodium chlorite appear to be much less drastic in their effect on cellulose and accordingly have found use in commercial bleaching processes. It has been claimed that the latter bleaches cotton goods without affecting oxycellulose formation.²⁰ In the acid region (i.e., chlorous acid), it oxidizes the aldehyde groups of modified celluloses to carboxyl groups without producing any other change. Thus, a dialdehyde type of oxycellulose produced by the action of periodic acid may be converted to a corresponding dicarboxylic acid by treatment with chlorous acid.²⁵

Finally, it should again be pointed out that, while the oxidation of cellulose by periodic acid is confined largely to the glycol group and that produced by nitrogen dioxide to the primary hydroxyl group of the glucose residue, other oxidizing agents are less specific and probably result in mixtures of the above reactions. This fact has seriously complicated attempts to elucidate the nature of the chemical reactions involved. Further advances in our understanding of the nature of the reactions of various oxidizing agents with cellulose will depend on a more accurate evaluation of the number, type, and location of the ketonic, aldehydic, or carboxylic acid groups which may be produced during oxycellulose formation.

Most oxidized celluloses undergo a striking change when they are treated with alkaline solutions. It is possible to completely remove the reducing groups by such a treatment to the extent that the remaining cellulose cannot be distinguished in this respect from unmodified cellulose. This may or may not be accompanied by an appreciable loss in weight, depending upon the type of oxidized cellulose in question. The effect of the so-called "alkali boil" on oxycelluloses has been demonstrated by many investigators. The effect on nitrocellulose fluidity is shown by a comparison of the results in Figures 9 and 10. In addition to a change in this property, a loss in strength occurs because of the scission of alkali-labile linkages, and the production of short chain fragments.

The periodic acid oxycelluloses are particularly characterized by their susceptibility to further attack by alkaline solutions. The alkali-sensitivity of these materials, as measured by solubility in hot dilute sodium hydroxide and by cuprammonium fluidity is about proportional to the

²⁰ Vincent, G. P., *et al.*, *Am. Dyestuff Repr.*, 30, 358 (1941).

content of aldehyde groups, at least in celluloses oxidized up to the extent of two glucose units in every hundred. It is of extreme interest that this sensitivity toward alkali is almost completely removed when the aldehyde groups are further oxidized to carboxyl groups²⁵ (by chlorous acid treatment). This same stabilization may be produced by the action of diazomethane on the periodate oxycellulose.²¹ Thus, the sensitivity of this type of oxidized cellulose does not depend solely on the rupture of the glucose ring between carbon atoms 2 and 3, but is related to the specific instability towards alkali of the dialdehyde formed during the oxidation.

The efficacy of alkaline solutions in producing further degradation of oxycelluloses is apparently not dependent solely on hydroxyl-ion concentrations. A comparison of the effects on the nitrocellulose fluidity of modified cellulose after treatment with sodium hydroxide and with cuprammonium hydroxide solutions of approximately the same hydroxyl-ion concentration showed that the former had a greater effect on an acid hypochlorite oxycellulose, while the latter had a greater effect on other types such as dichromate-oxalic acid oxycelluloses. The effects of other basic compounds, such as Triton F (dibenzyltrimethylammonium hydroxide), Triton B (benzyltrimethylammonium hydroxide), and cupriethylenediamine (all of which have been used for fluidity determinations), on the fluidity characteristics of modified celluloses have also been investigated. The degrading action of Triton F on alkali-sensitive modified celluloses appears to be similar to that of the inorganic alkalis. The fluidity in this solvent, unlike that in cuprammonium, is said to be a measure of the total chemical deterioration of the cellulose; that is, the solvent completely ruptures all alkali-labile linkages.

Although oxycellulose formation is in many cases accompanied by a decrease in the strength of the fibrous cellulose, the use of strength measurements as a measure of extent of oxidation may be misleading. This follows from the above discussion of the action of specific oxidizing agents in which it was pointed out that reducing oxycelluloses, such as those produced by periodic acid, may show little if any loss in strength although an appreciable amount of oxidation has occurred.

Acidic oxycelluloses, such as those produced by alkaline hypochlorite or by nitrogen dioxide, also vary in properties depending on the oxidizing agents and the conditions of oxidation. Nitrogen dioxide oxycelluloses which have carboxyl contents of 13% and above (theoretical for complete oxidation of primary alcoholic groups = 25.5%) are completely soluble in dilute aqueous solutions of sodium hydroxide, ammonia, sodium carbonate, and pyridine. The soluble salts formed with these bases may be precipitated by alcohol or other water-miscible nonsolvents. With polyvalent ions such as barium, insoluble salts are formed. The copper

²¹ Reeves, R. E., *Ind. Eng. Chem. Ind. Ed.*, **35**, 1218 (1943).

numbers of these oxycelluloses, which presumably should be low, are indeed very high; a sample which is completely oxidized gives a value which is theoretical for anhydroglucuronic acid calculated on the basis of the reducing power of one aldehyde group for each uronic acid residue. These results, as well as those obtained with incompletely oxidized materials, indicate that the copper number has no significance in respect to the oxycelluloses of this type, but rather that reducing groups are formed during degradation in the alkaline copper solutions used in the copper number method. That the carboxyl groups produced in oxidation of cellulose by nitrogen dioxide are of the uronic type is shown by the quantitative evolution of carbon dioxide when the material is boiled in hydrochloric acid. Of interest in this connection is the fact that the carboxyl groups produced by the action of chlorous acid on dialdehyde oxycellulose are not decarboxylated by boiling hydrochloric acid. Thus, a method for the partial allocation of carboxyl groups to their position in the glucose residues of oxidized celluloses is available.⁸²

3. EFFECT OF HEAT ON CELLULOSE

The difficulties involved in establishing the course of the chemical degradation of cellulose by heat are emphasized by the lack of specific information on the subject. Work has largely been limited to discussions of the properties of celluloses degraded by this means. As in the instance of other agents which produce degradation, the rate of breakdown is a function of a number of possible variables. Perhaps the greatest single factor influencing the extent of damage under a given set of conditions is the duration of heating. Thus, prolonged exposure at low temperatures may have a greater effect than exposure at high temperatures for shorter periods of time. The magnitude of the effect may be judged by the loss in breaking strength, rise in fluidity, increase in content of reducing groups, and increase in solubility in alkali.

The first noticeable result of the effect of heat on cellulosic materials is the loss of water. Below temperatures of 140° C. and a total time of heating of four hours no great changes appear to occur.⁸³ Some recent work,⁸⁴ however, has shown relatively small but measurable increases in solubility in alkali and copper number at lower temperatures during short intervals of heating.

The degradation is slower in the absence of oxygen, which indicates that the initial stages of breakdown, at least, include oxidative destruction.

⁸² Rutherford, H. A., Minor, F. W., and Harris, M. In preparation for publication.

⁸³ Doree, C., "The Methods of Cellulose Chemistry." D. Van Nostrand Co. (1933).

⁸⁴ Haas, H., *Kunstseide und Zellwolle*, 21, 88 (1930); Lewis, H. F., *Paper Trade J.*, 95, 29 (1932).

Continued heating, however, even in the absence of oxygen, leads to deterioration of the cellulose.

Stamm and Hansen⁸⁵ have postulated the formation of ether cross linkages to explain the decrease in affinity for water and in the ability to swell brought about by heating. While this hypothesis appears to explain a number of properties of celluloses after exposure to heat, there is no chemical evidence at hand to support the suggestion.

Other factors which influence the rate of tendering by heat are initial moisture content of the cellulose and of the surrounding atmosphere, the presence of impurities and the extent of pre-modification with respect to both hydrolysis and oxidation. Most regenerated celluloses, which have a low average chain length as compared with native cellulose, show rapid loss in strength under the influence of heat.

In a recent study of effects of drying conditions on the properties of textile yarns, it was shown that the "quality index" (defined as the percentage of the original breaking strength retained after drying multiplied by the percentage of the original elongation retained after drying) of cellulosic fibers decreases either as the temperature is increased or as the moisture content of the surrounding atmosphere is increased. The deterioration as measured by the fluidity method is shown in Figure 11. Both the breaking strength and fluidity of the purified cotton and the viscose rayon (Figure 12) appear to be functions of the relative humidity at which the samples are exposed. The damage is greater at a high humidity. In addition to a greater stability toward heat, cellulose acetate does not show the moisture sensitivity exhibited by the other two cellulosic materials.

It is apparent in the foregoing pages that the normal reactions of cellulose, occurring at or near room temperature, are directly related to the complex configurations of the cellulose molecule. A great deal is known about the nature and kinetics of these reactions. In contrast, at moderately elevated temperatures, the reactions of cellulose are appreciably more obscure and much less experimental data is available for verification of theoretical considerations. Finally, in the range of temperatures approaching that of a flaming fabric, the theoretical aspects of the degradation reactions become almost hopelessly complex and any truly fundamental consideration of mechanisms must rely on the simpler chemical reactions as discussed in the preceding section. A thorough understanding of these relationships will enable at least a partial extrapolation into the range of temperatures dealt with in the pyrolysis and combustion experiments which follow.

⁸⁵ Stamm, A. J., and Hansen, L. A., *Ind. Eng. Chem.*, 29, 831 (1937).

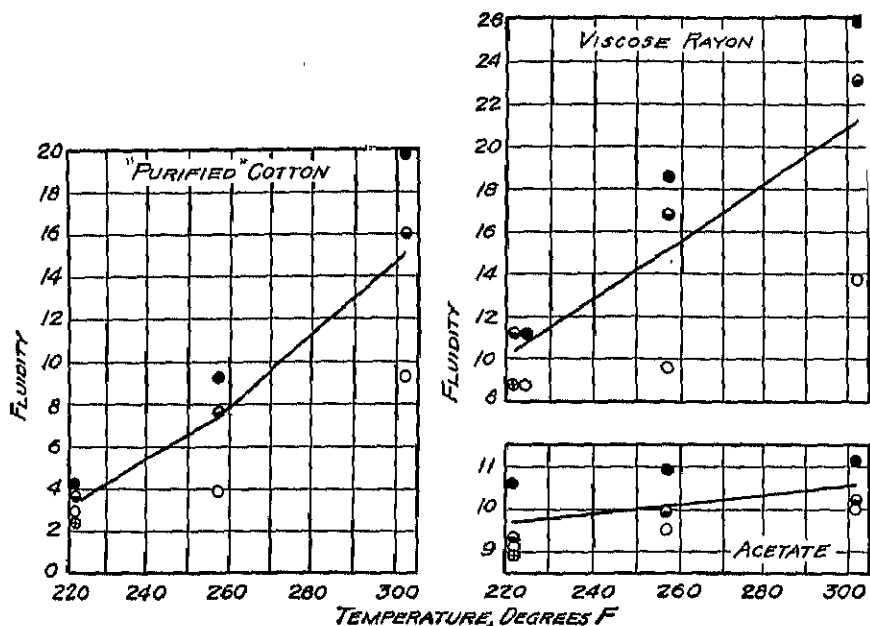


Figure 11. Effect of heat on the fluidity of yarns at low (○), medium (◐), and high (●) humidities; ⊕ represents initial fluidity. (Wiegink⁸⁰)

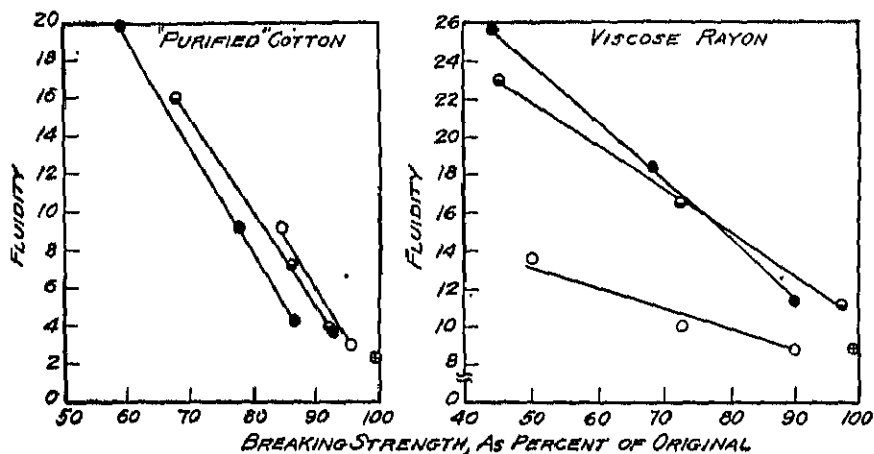


Figure 12. Relationship between fluidity and breaking strength of yarns which have been dried at low (○), medium (◐), and high (●) humidities; ⊕ represents initial relationship. (Wiegink⁸⁰)

⁸⁰ Wiegink, J. G., *J. Research Natl. Bur. Standards*, 25, 435 (1940).

C. PYROLYSIS REACTIONS

S. Coppick

When cellulosic materials are heated at high temperatures in the absence of air, a rapid, typically pyrolytic reaction ensues. At least two additional phases are added to the system, which finally consists of a solid char, a liquid distillate, and a gaseous fraction. As would be expected, the rates of formation and ratios of the various product-phases depend to a great extent upon the conditions of the experiment and the precautions taken to isolate the initial products from the reaction mixture as soon as they are formed. Failure in rapid isolation and separation of these phases results principally in further cracking of some of the liquids to give additional amounts of solid and gases. In researches designed to determine the path of the primary breakdown of the cellulose molecule, it is therefore advisable to consider quite carefully the conditions under which the pyrolysis is performed.

Although pyrolytic disintegration proceeds quite freely by exclusion of the air via an inert gas such as nitrogen or carbon dioxide, it is preferable to carry out the decomposition at reduced pressure to facilitate the distillation of the high molecular weight products. The most readily adaptable and simplest approach is then by means of vacuum distillation in a closed system. Adaption of the principles of molecular distillation also aid in the isolation of the primary products of the reaction, and is readily accomplished by a condensing surface of high capacity as close as possible to the surface of the pyrolytic charge. The use of downward distillation rather than the normal, where some refluxing always occurs, is additionally favorable to removal of primary dissociation products from the ensuing reaction.

Adaption of these principles to a simple workable apparatus is demonstrated in the following design shown in Figure 13. Its efficiency is comparatively high, since yields of from 70 to 80% of liquid phases may be obtained from pure cellulose. This aqueous distillate contains the tarry products which are isolated by drying at 105° C., several hours being sufficient to attain a constant weight which is not appreciably affected by further drying for periods as long as 36 hours. Purified cotton normally yields about 50 to 55% of the dried tar. This material is easily removed by solution in methanol to facilitate determination of the char yield, the wet gas being determined by difference from the original charge in the bulb.

The effect of temperature on the pyrolysis of cotton is likewise followed most conveniently by observance of tar yields. When the initial absolute pressure in the system is of the order of magnitude of about 20

millimeters of mercury, and the temperature is increased above the cellulose decomposition point, the reaction becomes more and more rapid until above 400° C. a constant rate is approached. This reaction velocity is observed as the rate at which the pressure change occurs in the system. The production of tarry products also increases with increasing tempera-

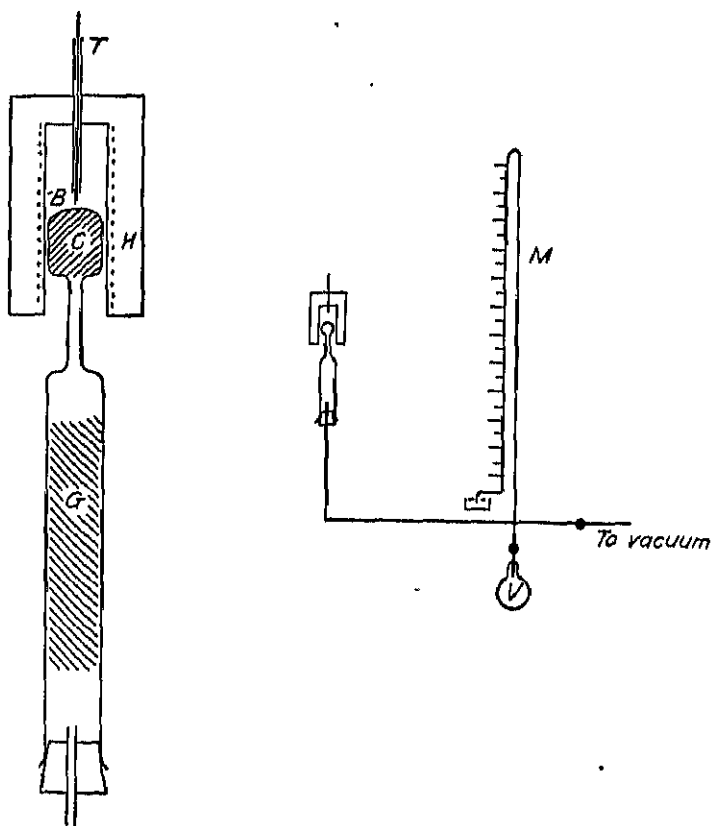


Figure 13. Equipment for pyrolytic investigations of the influence of retardants on the thermal decomposition of cellulose.

T: thermocouple; *B*: bulb from 1 by 8 inch test tube; *H*: heater; *C*: cotton; *G*: fiber-glass; *M*: manometer; *V*: volume of 500 cc.

ture, the dried yields at various temperatures being: at 300°, 33%; at 350°, 48%; at 400°, 52%; at 450°, 52%; and at 500°, 50%. Since burning fabric has been shown to attain a temperature in the vicinity of 500° C., and since the pyrolytic degradation appears to proceed at a constant rate in this range, it would seem that these conditions are admirably suitable for studies relating to the initial stages of the flaming decomposition reaction.

The absolute pressure in the system would be expected to exert several directing influences on the pyrolysis, higher pressures inducing further cracking of the tarry products as well as favoring their secondary oxidation. At 500° C. it is observed that as the initial absolute pressure is decreased below 600 millimeters of mercury, the tar yield is increased slowly from 40% until at starting pressures of 20 millimeters the yield has increased to 52%, which is not appreciably increased by additional reductions of the initial pressure.

Under these latter conditions, the last independent variable, pyrolysis time, is not critical. During the first two minutes of heating an induction period is observed which is associated with the thermal conduction of the system, as indicated by its dependence upon the initiating temperature. For the next two minutes the reaction proceeds very rapidly with the evolution of tarry and gaseous products, and is essentially complete at the end of the fifth minute, the pressure in the system rising only very slowly until about the tenth or fifteenth minute where it becomes practically constant. Hence, the conditions of 500° C., 20 mm. of mercury and 15 minutes of pyrolysis time are ideal for comparative studies.

When a number of the well-known soluble salts which are effective as fire retardants are added to cotton, certain well-defined changes are observed in both the rate and course of the pyrolysis. The induction heating period is decreased with increasing addition of the salt, probably by increased thermal conductance, and the velocity of the gas production is increased appreciably by the addition of small amounts of these salts. However, after the addition of about 10% of the retardants, the rate and quantity of gas evolution becomes practically constant at about twice its original value, as indicated by the rate and amount of mercury fall in the manometric system. Moreover, it is not only the effective flame retardants that exhibited this effect, for almost identical behavior is observed for inert materials such as sodium and potassium chloride which have little or no effect on the flaming characteristics of cellulose. It would appear that this ability of salts to increase both the rate and quantity of the gas phase resulting from the primary disintegration of cellulose is not specific for flame-retarding materials, but is a general phenomenon probably associated with a secondary independent reaction.

The other two pyrolysis phases, however, bear a more direct relationship to the flame-retarding properties of the salts. With the addition to cellulose of as little as 5% of a typical retardant such as diammonium phosphate, the tarry distillates are reduced in yield from about 55% to approximately 5% of the weight of the original cotton. On the other hand, a similar addition of an inert or poorly effective material such as sodium chloride only results in the reduction of the tarry products to a yield of about 30%. The ability to effect large decreases in the production of these tarry primary disintegration products appears to be specific for fire-

retarding materials. The sulfamates, sulfates and phosphates as their ammonium salts as well as the effective borax-boric acid mixture exhibit various efficiencies as depicted in Figure 14. In some cases, however, par-

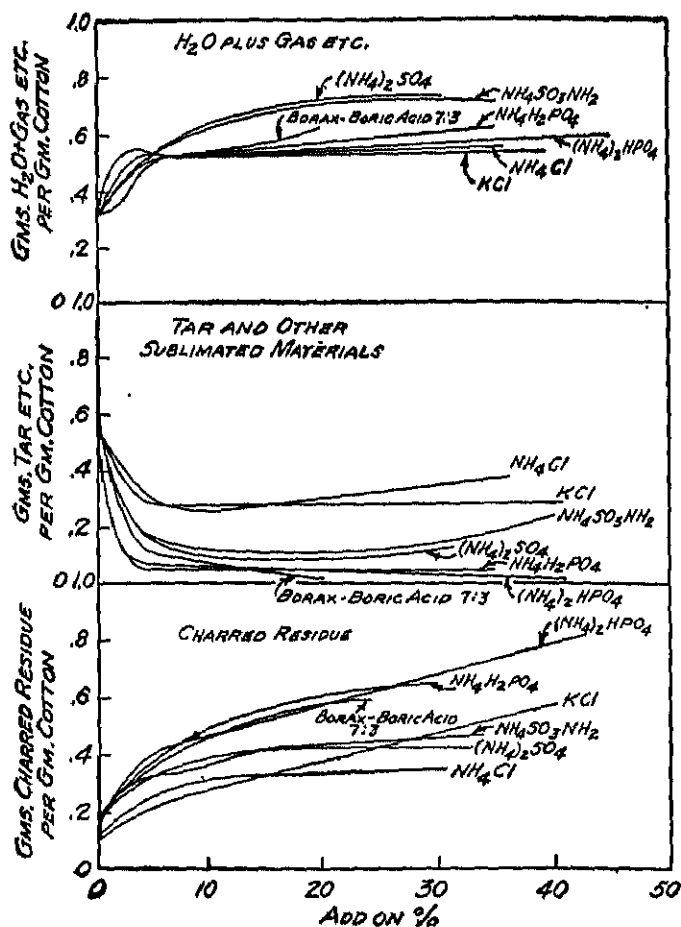


Figure 14. The influence of retardants on the quantity of the various phases resulting from the pyrolysis of cotton.

ticularly with the sulfamates, a true picture of the effectiveness cannot be obtained since the retardant itself decomposes and sublimes rather readily, and the tarry distillation products are contaminated with this sublimate. The maximum efficiencies of the various salts in tar-reducing capacity occur for the addition of the first 5 to 10% of material added to cotton, further additions having little or no subsequent effect. This is a particularly interesting behavior since it is well known that with the addition of these magnitudes of the effective retardants to a fabric, flame

propagation suddenly ceases and the amount of salt required for this protection is rather critical.

The amount of the third and last phase produced during pyrolysis, *i.e.*, the charred residue, likewise serves as a criterion of the flame-retarding efficiencies of various salts. The effective materials greatly increase the quantity of this char for small additions of the retardant. For instance the addition of 5% of the borax-boric acid mixture results in a char yield increase from the normal 10% to about 40%, while the ineffective potassium chloride increases the char yield only to 20% by a similar 5% addition of the salt. It is to be remembered here that the charred residue consists not only of the products from the cotton, but also of those from the retardant. In most cases these may be separated by hot water extraction of the residues, to leave a true char from the cellulose. In the case cited above, extraction shows that the true char from cotton treated with potassium chloride never exceeds a yield of 14% while that from the borax-boric acid mixture on cotton rises rapidly to 35% for less than 10% addition of the salts and finally becomes approximately constant in the neighborhood of 40% yield irrespective of the amount of retardant added to the cellulose.

In similar pyrolytic experiments on cotton fabrics it is observed that the tar production of the untreated material, although high, is not quite as great as that obtained with the absorbent cotton used entirely in the above. For the fabric, tar yields rarely exceed 42%, and depend somewhat upon whether the yardage is in the grey, desized, or dyed state. These effects parallel to some extent actual inflammability as measured by flame propagation rates in the various fabrics and with absorbent cotton.

Commercially treated fabrics with good flame-retarding properties behave very similarly to the experimentally flame-proofed absorbent cotton. The pyrolytic tars are low in yield and usually constitute from 5 to 10% of the original cellulose content of the material. The relative flame protection afforded by these treatments, as determined by practical flame tests, is nearly always in accord with their low tar-producing capacity. However, in a number of cases contamination of the tar renders its accurate determination difficult or impossible. This is particularly the case with treatments of the antimony oxide-chlorinated compound type, where sublimation of both constituents along with the tars takes place to such an extent that an apparent tar value of 27% is obtained for the fabric. This is certainly inconsistent with its performance.

From the above it may be concluded that the primary effect of flame-retarding chemicals is to alter the products resulting from the initial thermal decomposition of the cellulose molecule. The greatest change occurs in the solid and liquid phases, the gas being augmented in quantity somewhat both by retardants and nonretardants. However, the magnitude

of the changes of tar and char products is directly related to the flame proofing efficiency of the added salt. It has been observed further that the tarry products are of a highly inflammable nature, are readily ignited and propagate a flame very rapidly when impregnated on glass-wool or asbestos fabric. It would appear then that these are the products most directly responsible for the flaming of cotton fabrics and that the main function of a retardant is to limit the production of these materials when the fabric is subjected to a flame source.

The over-all effect of the efficient retardants appears to be the direction of the initial disintegration toward products in the solid phase rather than along the lines of the normal and partial decomposition toward liquid phase fragments which vaporize, and on admixture with the oxygen of the air are readily ignited and constitute the flame. The prime cause for these effects is not considered here, but is postponed and will appear in the section devoted to the theoretical concepts postulated to explain the underlying principles involved in retardant action. All that is intended here is to delve as deeply as possible into the decomposition reactions in an effort to bring to light conclusively the primary effects of retardants on cellulose at high temperatures.

D. COMBUSTION REACTIONS

S. Coppick

The burning of organic materials in general is a very complex process, involving a great number of steps wherein the material undergoes successively many stages of disintegration and oxidation. A study of the final end products leads to very little information regarding the intermediates which pass rapidly toward the lower energy levels and in the limit appear as carbon dioxide and water. It is of course well known that the efficiency of the process is directly concerned with the rate of oxygen supply and its concentration at the combustion source, which determine the extent of the energy drop in the final stages of the series of reactions. Thus, normally, the combustion of cellulose results in the formation of carbon monoxide as well as carbon dioxide and water. Smaller quantities of hydrocarbons such as methane sometimes occur but only under very adverse combustion conditions. Hence, investigations of the effect of retardants on the completed reaction are unprofitable, the products being practically identical for both treated and untreated cellulose and critically dependent upon the conditions of the oxidation. The only differences appear to be in the rate of the process as measured by the velocity at which a flame propagates throughout the mass of the material, and the extent to which the transfer from solid to gas phases occurs. This is measured very readily as the yield of residue remaining after ignition.

When flame propagation rates are reduced to zero by the application of an efficient retardant an impasse is reached, since it is here desirable to study a reaction which normally does not proceed. The approach must then be directed toward forcing the reaction in order to elucidate its normal inhibition. Moreover, during the thermal oxidation of cellulose three general reaction phenomena are observed, both the rate and extent of which depend not only upon the amount of the retardant added but also upon its nature. These are first, the propagation or chain reaction by which the incandescent gas meniscus is transported from one point to another. This reaction proceeds at velocities dependent upon a number of factors which include the state of division of the cellulose, the amount of retardant added, and the conditions of the experiment including the direction in which the flame travels. During horizontal flame propagation along a fabric, a deceleration is observed, while for vertical travel the velocity is greatly accelerated. Practically constant rates occur at angular directions in the neighborhood of from 30 to 45° to the horizontal.

As flame velocities are reduced by successive additions of an efficient retardant a critical point is usually reached at which the rate becomes zero. Here one enters the range of the forced reaction which is the second phase of flameproofing and involves the rate and extent of thermal decomposition of cellulose while in the presence of an instigating flame source. On removal of this source, provided the fabric has been efficiently treated, no chain reaction proceeds, although the flaming fabric may augment the source while the latter is present. This is the action which is finally observed as char length or area in practical flame tests or as the weight loss due to the decomposition.

The third and last general reaction phenomenon observed in the thermal oxidation of cellulose is the secondary exothermic decomposition of the solid products produced by either of the other two reactions. This is the flameless combustion of the char identified as afterglow, and appears to be entirely independent of the flaming reaction, since it may be produced or eliminated at will by judicious choice of both the quantity and type of retardant employed.

To further elucidate the primary effects which retardants have on the thermal oxidation of cellulose, it is advisable that the reaction be quenched during its preliminary stages for reasons similar to those stated in the previous section. The stipulation that the fragmentary decomposition products should be removed rapidly from the heat source appears to be even more critical when oxygen is present in the system. The arrangement of Figure 15 is adequate and is similar in principle to that previously used in vacuum studies, with the exception that the upper end of the tube is open to the atmosphere. Cellulosic material is placed in the upper bulb of the tube which is then inserted in the heater. The air drawn into the system via the aspirator is proheated on passage between the combustion

tube and the internal surface of the heater, and proceeding downward through the cellulose sweeps the fragmentary disintegration products t

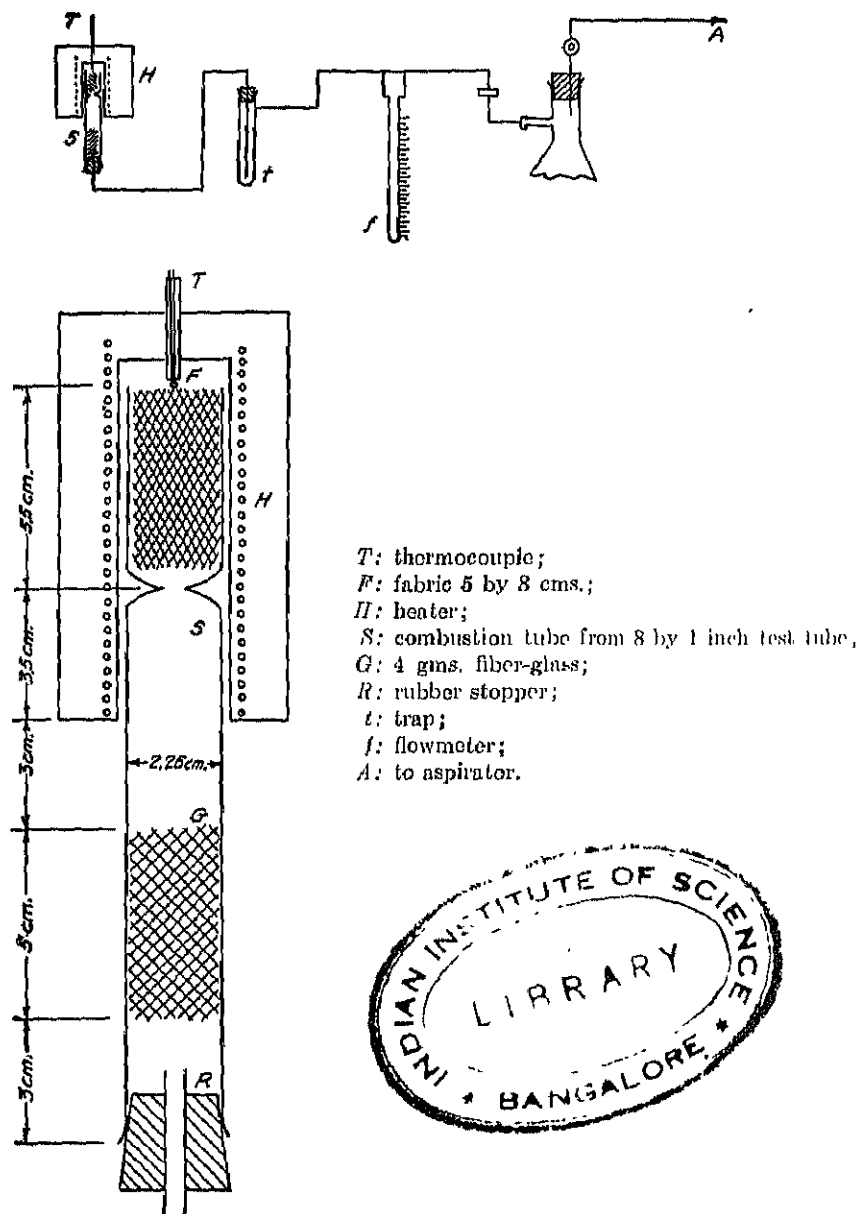


Figure 15. Equipment for controlled combustion investigations of the influence of retardants on the thermal decomposition of cellulose.

the large surface of the fiberglass condenser where they are absorbed. The determination of the various combustion phases is carried out as be-

fore. Cessation of the combustion at various intervals of time is accomplished by removing the tube from the heater and cutting off the air supply by inserting an asbestos stopper in the upper end of the combustion bulb.

Preliminary studies on absorbent cotton show that the rate of air flow is a rather critical factor in determining the ratio of the various phases formed at 500° C. Velocities such that less than 40 cc. of air per minute pass through the system are insufficient to give the liquid decomposition products the required directional influence to permit their accurate analysis, and their secondary cracking to solid and gas phases is indicated by the increased quantities of these products. Increasing the air flow from zero to 40 cc. per minute results in a dried tar yield increase from 9 to 40% of the original cotton. This yield is not changed by further increasing the air flow. However, the oxygen input represented by the rate of 40 cc. of air per minute is insufficient to promote a conveniently measurable rate for the secondary oxidation of the charred residue, which still retains a yield of about 10% even after 15 minutes of combustion at 500° C. Under these conditions the oxidation rate is gradually increased with increasing air input until at about 100 cc. per minute combustion of the char is complete in 15 minutes. To insure inclusion of an adequate safety factor it is preferable to carry out the oxidation at air input values considerably in excess of this minimum, and 180 cc. per minute appears to be satisfactory for differentiation purposes in a large number of treated and untreated cottons. The following experiments adopt these standard conditions. For comparative determination of the flaming tendencies of fabrics it is convenient to use a propagation rate for those of easy ignition, while afterflaming and char dimensions characterize those whose propagation rate is reduced to a negligible value. These flame tests are described fully in a later chapter³⁷ devoted to testing procedures.

The influence of retardants on the products of the combustion of absorbent cotton is very similar to that found for the decomposition in vacuo. With addition of the well-known and effective salts such as the borax-boric acid mixture, the water-gas fraction is increased, the tarry products decreased and the charred residues increased. The changes in the amounts of the various phases are again most pronounced in the region of the addition of up to 5 to 10% of these salts, which is again in agreement with their known flame retardation performance. In the case of the ineffective salts such as potassium chloride, the gaseous products are increased to an extent equal to that observed for very effective materials, but the quantities of tar and char products are quite different.

A typical set of data is shown in Figure 16, where distinction is made between the water-soluble and insoluble constituents of both the charred residue and the tarry distillate. Flame retardants such as the borax-boric

³⁷ Chapter IV, Section B-2, Flame Tests

acid mixture, calcium chloride or ammonium molybdate demonstrate ability to reduce the inflammable tars from a normal yield value of to less than 5% of the original cotton. On the other hand, the poorly effective potassium chloride seems unable to effect a tar reduction.

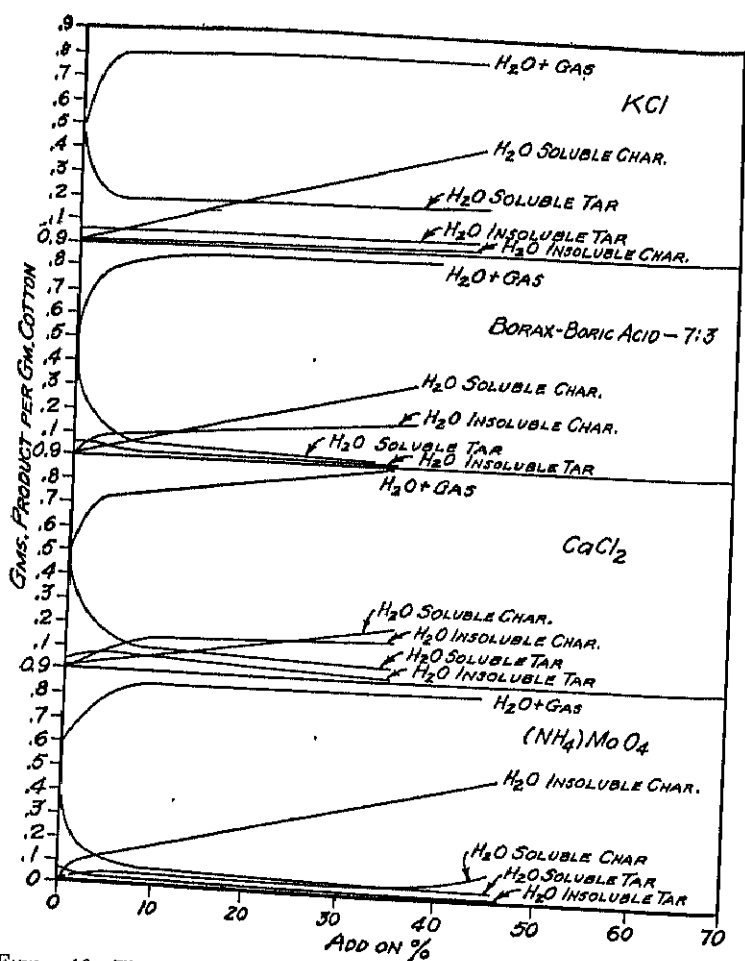


Figure 16. The influence of retardants on the quantity of the various phases resulting from the controlled combustion of cotton.

to less than 20% yield irrespective of the amount added to the fiber. Similar effects are also observed with woven fabrics.

Some peculiar behavior is observed when either small amounts of water-soluble retardants are added to cotton fabrics or when effective treated materials are leached with water until only slight traces of the original salts remain in the cell wall. It appears that these small amounts actually increase the velocity with which a flame will propagate along the

fabric surface, although the addition of larger quantities reduces this rate, which in the limit becomes zero and the fabric is then substantially flameproofed. Investigations on the tar production in the range of increased inflammability show that although the amount of these volatile fragments is decreased slightly below the quantities obtained from untreated fabrics, these tars are more easily produced. Thus the effects of some retardants are competitive in nature, *i.e.*, a reduction in amount of fuel supply as tarry fragments but also an increase in their rate of generation at a given temperature. These opposing influences may either increase or decrease the tendency to propagate the flaming reaction and depend upon the concentration of the retardant in the fabric. Fortunately, however, the concentration coefficients for the extent and rate of the reactions are entirely different so that after the addition of more than 0.5% of these retardants the rate of tar production ceases to be the controlling factor and its lower quantity begins to exert a dominating influence which appears as a net reduction of the propagation velocity of the flame. These effects are shown in Table 2, which indicate the enhanced inflam-

Table 2. Effect of Small Amounts of Retardants on the Tar Production and Inflammability of Fabrics

Retardant	Add-On %	No. of 15-min. Static Water Leachings	Tar mgs/cm ² of Fabric	Flame Rate in/sec	Time to Maximum Tar Production min.
Ammonium	0	—	11.88	.103	4
Dihydrogen	0.05	—	9.92	.164	3
Phosphate	0.1	—	9.42	.218	2
	0.25	—	10.16	.210	2
	0.5	—	6.68	.137	2
	1.0	—	4.60	.087	2
Commercial	0	—	11.88	.119	4
Sulfamate-	0.5	—	10.15	.197	4
Phosphate	0.1	—	10.37	.203	3.5
Mixture	0.25	—	9.16	.187	3
	0.5	—	6.75	.153	3
	1.0	—	5.23	.103	3
Ammonium	15	0	—	0	—
Dihydrogen		1	—	.105	—
Phosphate		2	—	.200	—
		3	—	.222	—
		4	—	.167	—
		5	—	.182	—
Commercial	15	0	—	0	—
Sulfamate-		1	—	.091	—
Phosphate		2	—	.222	—
Mixture		3	—	.200	—
		4	—	.208	—
		5	—	.143	—
Desized Twill (untreated)	0	0	—	.133	—

mability induced by small amounts of either the phosphate or sulfamate type of retardants, whether traces of these salts are added directly or a the residual amounts remaining after the bulk of the retardant in an effectively flameproofed fabric has been removed by leaching.

The increased addition of the effective salts to fabrics finally result in a reduction of the inflammable tarry products below the threshold value required for self-sustaining of the flaming reaction and its propagation ceases. Further additions reduce the interval between removal of the instigating source and the cessation of the flaming reaction, until this in turn reaches a zero limiting value. Still further addition of the retardant with its subsequent tar-reducing tendency promotes the reduction of fabric flaming even in the presence of the instigating source, which appears as the lessening of quantity or area of fabric destroyed by a flame of standard aspect and duration, *i.e.*, a reduced char dimension. This very close correlation between the flaming performance of fabrics and their tar production capacity is apparent from Table 3, which includes data on the phosphate, sulfamate and borate types of retardants. It is seen that the

Table 3. Correlation Between the Tarry Products from Controlled Combustion and the Burning Characteristics of Fabrics

Fabric	Retardant	Add-On %	Tar from Combustion mg/cm ² of Fabric	Flame Rate in/sec	Vert. After-flaming sec.	Vert. Char. Length in.
Desized Grey Goods	None	0	15.2	.164	> 20	12
Desized Twill (dyed)	"	0	12.7	.151	> 20	12
Regular Twill	"	0	9.9	.135	> 20	12
Grey Goods (sized)	"	0	5.6	.116	> 20	12
Desized Twill	Borax:	0.2	8.6	.111	> 20	12
	Boric Acid	1.3	5.2	.100	18	12
	7 : 3	1.6	4.3	.069	19	12
	"	2.0	3.8	.056	15	12
	"	3.5	2.5	0	7	5.7
	"	6.5	1.3	0	0	3.7
	"	13.6	1.1	0	0	2.1
Desized Twill	Ammonium	0.7	3.5	.085	> 20	12
	Dihydrogen	1.1	3.2	.050	> 20	12
	Phosphate	4.8	2.3	0	> 20	12
	"	5.6	2.1	0	1	6.7
	"	8.2	2.3	0	0	5.7
	"	18.3	2.4	0	0	3.2
Desized Twill	Commercial	1.0	5.2	.103	> 20	12
	Sulfamate-	2.1	3.8	.096	> 20	12
	Phosphate	3.1	3.2	0	> 20	12
	Mixture	5.1	2.8	0	> 20	12
	"	9.6	2.2	0	0	3.9
	"	18.8	1.5	0	0	2.7
	"	31.2	1.0	0	0	2.7
	"	41.8	3.5	0	0	2.6

borax-boric acid mixture does not exhibit the behavior previously shown for the other two retardant types. The addition of 0.2% of this mixture gives no enhanced flame-spreading velocity such as demonstrated by the sulfamate-phosphate retardant mixture and by ammonium phosphate alone.

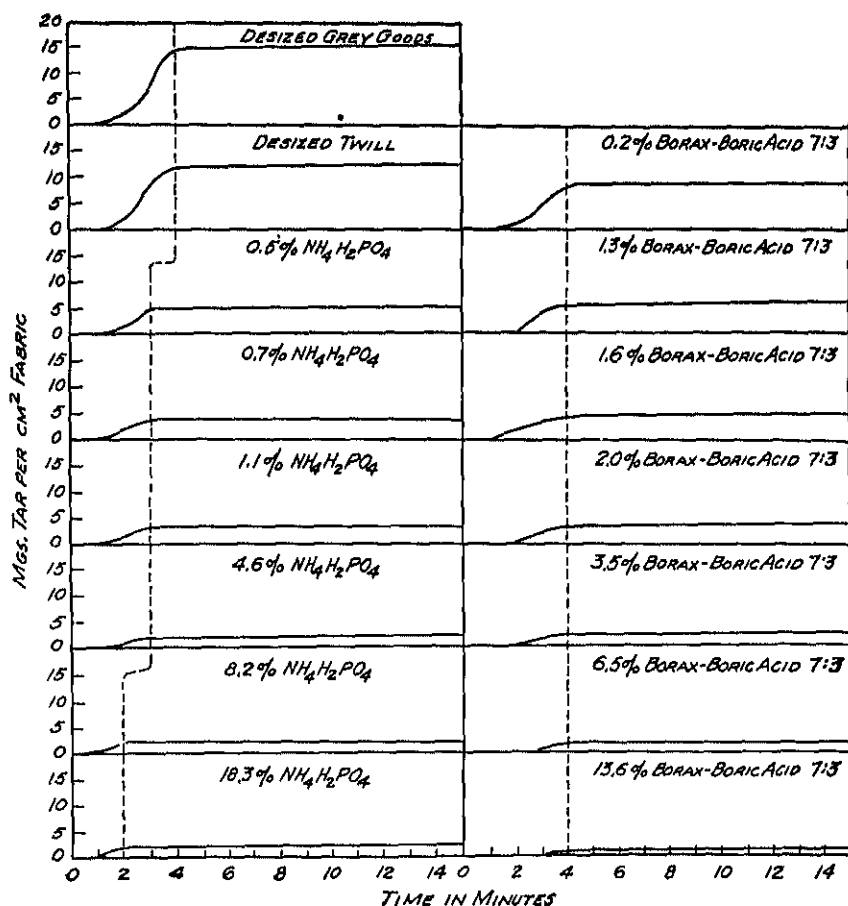


Figure 17. The effect of the phosphate and borate types of retardants on the rate of production of volatile cellulosic fragments during the controlled combustion of cotton fabrics. (The per cent values are those added to desized twill.)

The reason for this anomalous behavior becomes apparent from kinetic studies on the degradation reaction. Interruption of the combustion at successive time intervals of one minute over the whole of the 15-minute oxidation period and measurement of tar production leads to the determination of the rate of the process. It should be remembered, however, that the experiment is not conducted entirely isothermally since an

induction period is necessitated wherein the fabric is raised over a 1 temperature gradient from room conditions to approximately 500°. With an untreated fabric, tar production does not begin until after first minute of exposure and proceeds at increasing velocity over the 1 minute with increasing charring of the fabric. During the third minute is evolved at its maximum velocity which appears to be constant for material and independent of the initiating temperature. The slower rate apparently is due to non-uniform attainment of the decomposition temperature, and less rapid decompositions at intermediate temperatures. As the reaction approaches completion toward the fourth minute the rate of tar production decreases and at the end of the fourth minute the amount of tar reaches a constant value, which is not affected by further increasing the combustion duration up to 15 minutes.

The effect of both the phosphate and borate mixture is quite similar as far as their influence on the quantities of the product are concerned although the borate appears to have a greater efficiency in tar reduction. However, their effect on the temperature coefficient and rate of the reaction appears to be entirely different, as demonstrated in Figure 16. With the phosphate retardant, the time interval over which tar is produced is reduced from three- to a one-minute period for successive additions up to 8% of the retardant and the reaction is then complete at the end of the second minute. In the case of the borate retardant, on the other hand, no change in the heating period required for completion of the tar generation reaction is observed, an interval of 4 minutes being required irrespective of the amount of these salts added to the fabric. Similar rate differences are found for the decomposition of the solid phase and it appears that the borate mixture has the advantage of not containing the two competitive factors of rate and extent of reaction, which render the phosphate a flame promoter in the low addition range. Rate changes for tar production, similar to those depicted in Figure 17 for the phosphate, have been observed for the commercial sulfamate-phosphate mixture, sulfamate alone, and permanently phosphated fabrics as well as for the 7:3:5 mixture of borax, boric acid and ammonium phosphate and appear to be associated with the strong acid type of retardant. Comparative charring of the fabric during the early stages of the combustion is seen in the photographs of Figure 18. These effects indicate that the two types of retardant function via somewhat different mechanisms.

E. THERMAL DECOMPOSITION PRODUCTS

S. Coppick

1. GAS PHASE PRODUCTS

In the previous sections devoted to the reactions ensuing during the pyrolysis and controlled combustion of cellulose and its retardant com-

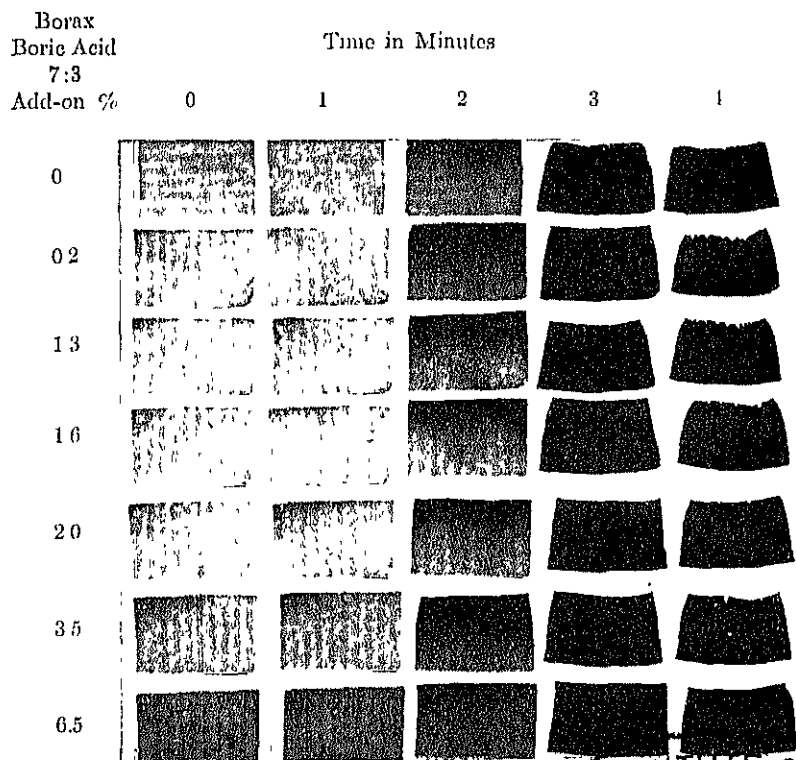
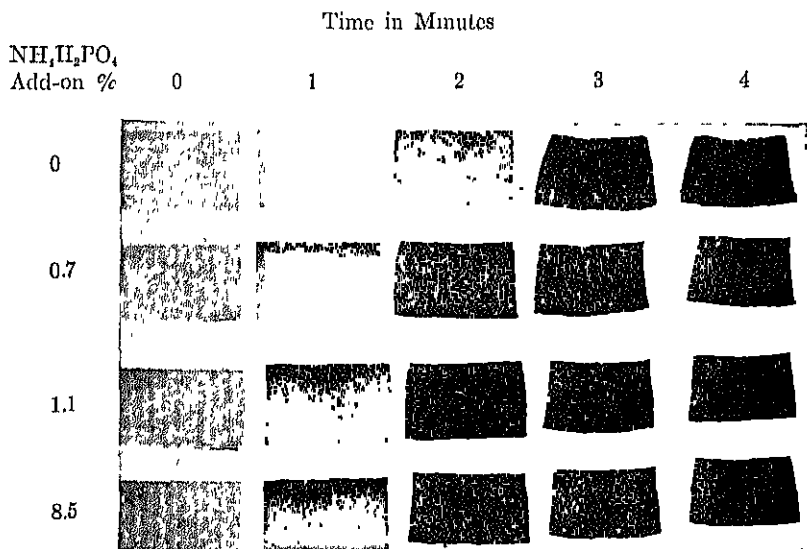
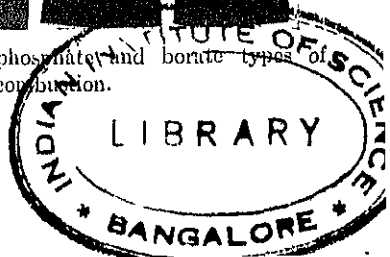


Figure 18. Comparative charring rates for the phosphate and borate types of retardants during controlled combustion.



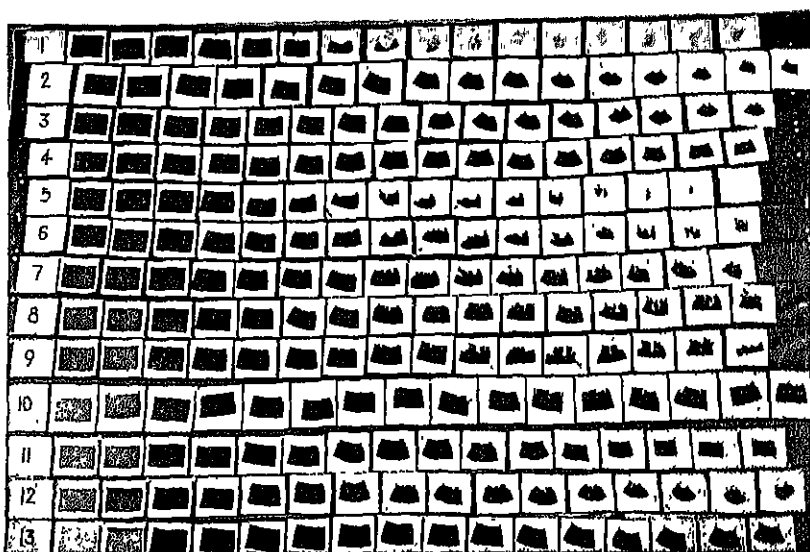


Figure 23. Charred residues at 1-minute intervals during the controlled combustion of fabrics.

1. Untreated
2. 0.7% Ammonium dihydrogen phosphate
3. 1.1% Ammonium dihydrogen phosphate
4. 8.5% Ammonium dihydrogen phosphate
5. 0.2% Borax:Boric acid::7:3
6. 1.3% Borax:Boric acid.:7:3
7. 1.6% Borax:Boric acid::7:3
8. 2.0% Borax:Boric acid :7:3
9. 3.5% Borax Boric acid: 7:3
10. 6.5% Borax:Boric acid::7:3
11. 8.2% Borax:Boric acid Ammonium dihydrogen phosphate::7:3:5
12. 8.5% Commercial sulfamate-phosphate mixture
13. 16% Commercial urea-phosphate type treatment



binations, it is seen that although the products in the gaseous phase are augmented both in amount and production rate, their values do not appear to be critically related to the flaming mechanism and its deceleration. Both retardants and non-retardants show very similar effects in enhancing the quantity of vapors and the velocity of their generation, but there still remains the possibility that the vapor composition might be variable.

It is to be remembered that in the previously described experiments the gas phase has always included the water produced in the decomposition. However, the determination of the dry gas phase is easily carried out by measurement of weight losses involved in experiments conducted via

Table 4. The Effect of Retardants on the Amount of Dry Gas Produced During the Pyrolysis of Fabrics
Treated with the Sulfamate-Phosphate Retardant System

Retardant	Add-On %	Pressure Increase mm. of Mercury	% by Wt.	Quantity of Gas mgs/cm ² of fabric
Ammonium	0	87	1.8	0.46
Dihydrogen	0.5	214	6.0	1.52
Phosphate	1.3	250	6.1	1.56
	3.1	258	6.4	1.63
	6.6	308	17.6	4.45
	17.2	258	14.5	3.19
Ammonium	0	87	1.8	0.46
Sulfamate	3.5	234	6.9	1.56
	4.1	376	11.0	2.80
	8.1	374	12.5	2.88
	12.7	519	15.8	4.49
	25.1	464	13.1	3.88
Commercial	0	87	1.8	0.46
Sulfamate-	2.1	263	6.0	1.54
Phosphate	3.1	332	8.7	2.20
Mixture	5.1	380	8.6	2.54
	9.0	385	9.9	2.54

modification of the equipment of Figure 13. Replacement of the glass wool in the sorption section of the condenser by a dehydrating agent ensures collection of both tarry and aqueous distillates. The rate of the process is observed as usual by the rate of pressure increase in the system, and the extent of the reaction by the total pressure increase when equilibrium is attained. The results for various retardant types added to cotton fabrics are given in Table 4, wherein the quantities of dried gas show effects with increasing retardant addition similar to those previously discussed for the saturated gas phase. The rate at which this phase is produced is increased substantially by relatively small additions of effective flame decelerants of the borate, phosphate and sulfamate type. In the neighborhood of about 5 to 10% addition of these salts the quantity and production rate become practically constant and even appear to pass

through a maximum, further additions of the retardant causing a slight reduction in the amount of gas.

Great changes in the flame-retarding characteristics of fabrics may be obtained by variations in a complex system involving the three components, borax, boric acid and ammonium phosphate. Investigation of the dry gas from the pyrolysis of fabric treated with various amounts of each of these components and their mixtures produce the results given in Table 5. It appears that the quantity augmentation of the dry gas phase is

Table 5. Dry Gas Variations in the Pyrolysis of Fabric Treated with Borax, Boric Acid and Their Mixtures

Retardant	Add-On %	Pressure Increase mm. of Mercury	% by Wt.	Quantity of Gas mg./cm ² of fabric	Vertical Afterflaming sec.
Boric Acid	0	212	1.75	0.47	> 20
	3.4	482	11.33	2.51	> 20
	5.4	437	8.85	2.27	> 20
	7.7	448	10.65	2.50	> 20
	10.4	435	8.77	2.26	> 20
	10.5	449	9.95	2.35	> 20
	13.0	472	9.23	2.38	> 20
Borax	0	212	1.8	0.46	> 20
	2.8	388	10.2	2.59	15
	5.4	400	10.4	2.62	3
	12.9	427	10.7	2.90	3
	20.3	413	10.7	3.01	3
	29.0	417	10.3	3.15	3
	34.5	419	9.1	3.01	0
Borax:	0	212	1.75	0.47	> 20
Boric Acid 7 : 3	2.5	492	10.42	2.61	18
	4.6	534	10.25	2.80	0
	8.4	553	10.80	2.97	0
	16.5	538	9.20	2.58	0
	30.1	564	8.99	2.82	0
	43.7	608	9.35	3.21	0
Borax:	0	212	1.75	0.47	> 20
Boric Acid: Ammonium Dihydrogen Phosphate 7 : 3 : 5	3.9	540	10.49	2.67	> 20
	5.6	482	8.75	2.37	> 20
	10.4	495	8.77	2.45	0
	19.2	524	8.13	2.70	0
	34.2	420	6.86	2.31	0
	59.9	515	6.96	2.48	0

a general phenomenon and bears little if any relation to the flaming characteristics of the fabric since the ineffective boric acid produces effects almost identical with those given by equal additions of either the fairly effective borax, the good three-component or the excellent two-component retardant system. The vertical afterflaming values characterize the relative burning properties of the various treated fabrics.

For more complete characterization of the gaseous phase produced during the pyrolysis of treated and untreated fabrics, the vapors must be isolated and subjected to the standard analytical procedures. A convenient and satisfactory system is shown in Figure 19, where the pyrolysis is carried out in a small bulb (shown inside the heater) over an adjustable mercury column in the pipette, B_1 . After completion of the reaction the heater is removed and the specimen bulb cooled. The sealed capillary point, p_1 , is then connected to the analytical system at P_2 via rubber tubing, and by breaking the capillary the gases may be transferred to B_2 ,

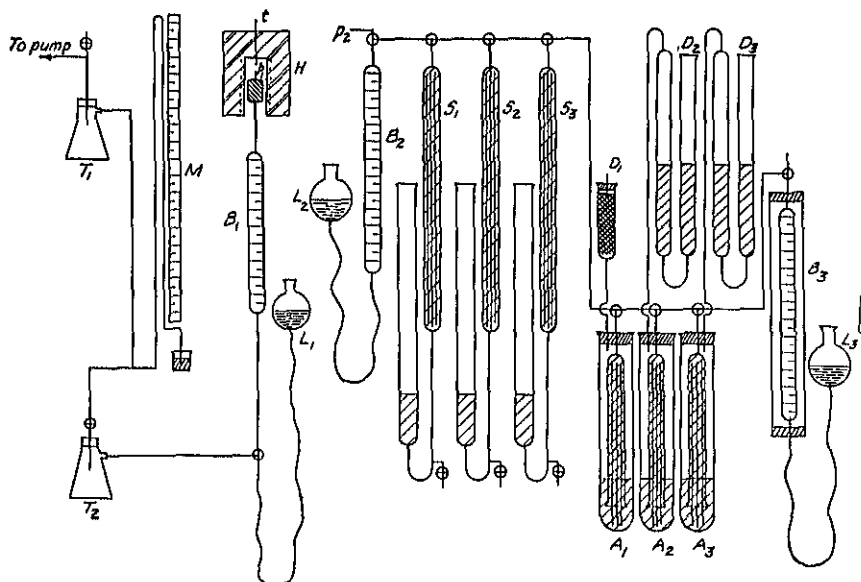


Figure 19 Equipment for the determination of the composition of the gas phase generated during the pyrolysis of cellulose in the presence of various retardants.

M : manometric system; T_1 , T_2 traps; H : heater; t : thermocouple, p_1 : sealed capillary on fabric bulb; B_1 , L_1 gas collecting system, B_2 , L_2 gas measuring system; P_2 : connection to analytical system; S_1 , S_2 , S_3 gas scrubbers, A_1 , A_2 , A_3 gas absorbers; D_1 : ascarite trap, D_2 , D_3 water traps, B_3 , L_3 Orsat burette system

where they are retained over mercury. The soluble constituents are determined by washing the gases in the three scrubbing sections, S_1 , S_2 and S_3 . On transfer to the burette, B_3 , where the saturated gas is maintained over water, its constitution is determined by selective absorption in the standard Orsat bulbs at A_1 , A_2 and A_3 . The Ascarite trap, D_1 , and water traps, D_2 and D_3 , protect the absorption liquids in A_1 , A_2 and A_3 from the outside atmosphere.

In the case of the controlled combustion of fabrics the products are identified by use of a modification of the equipment shown in Figure 15. The inclusion of U-tubes containing "Drierite" and "Ascarite" in series

with the tar absorber facilitates the determination of the aqueous CO_2 constituents.

Investigation of the total pyrolytic gas phase resulting from the composition of fabric treated with the commercial phosphate and silicate mixture indicates as usual an increase in the amounts produced increasing addition of the retardant. This increase is not at all linear with the add-on but assumes a maximum in the vicinity of a 10% addition. Similar effects are observed for each of the constituents alone applied to fabrics. Moreover, it is observed that the augmentation is not entirely to vapors arising from the decomposition of the retardant, as on scrubbing the gases from fabrics the same maxima occur, while if retardants are added to glass fiber the resulting vapors are all dissolved in the scrubbing process. The effects appear to be associated with the actual course of the decomposition of the cellulose itself, the retardant exerting more of a directing rather than a contributing effect to this phase.

The sulfamate-phosphate system does not lend itself very well to studies of this kind due to the complexity of the sulfur compounds evolved during the decomposition. A much simpler system from an analytical point of view is found in the borate mixtures on which a very detailed investigation is shown by the data of Table 6, where the components and mixtures of the retardant system are compared with sodium chloride.

It appears that the pyrolytic gases show the same type of behavior previously demonstrated in the sulfamate-phosphate system, the retardant increasing the total quantity of this phase to about twice its normal value. These gases contain about 35% of readily soluble constituents which are very probably the lower molecular weight aldehydes and acids, 35% CO , 15% hydrocarbons and about 15% CO_2 , the latter being the only non-flammable constituent. With the addition of the retardants of various flame-retarding efficiencies, the distribution of the quantities of the inflammable constituents varies somewhat, but the non-flammable CO_2 constituent remains approximately constant. There appears to be no radical difference in the over-all composition as one proceeds from the ineffective sodium chloride and boric acid through the fairly effective borax to the very efficient 7:3 mixture. The general indication is that the gas phase maintains approximately constant flammability composition but increases in amount on the addition of any salt to the fabric.

Similar effects are observed in the data accumulated in combustion studies. Here, due to presence of air during the thermal decomposition some of the flammable gases produced in the primary dissociation are further oxidized to CO_2 , thus this component increases with increased gas production. However, the amount arising from fabric treated with NaCl is about the same as that from fabric treated with the effective retardants. The same appears to be true of the aqueous constituent which increases

Table 6. The Effect of Various Materials on the Composition of the Gases Evolved During the Pyrolysis of Cotton Fabrics

Retardant	Add-On %	Total Gas cc/cm ² of fabric	Gas Components (% by volume)				CO ₂
			H ₂ O Solubles aldehydes, acids, etc.	CO	Hydro- carbons, etc.	Total Inflam- mables	
Sodium Chloride	0	1.04	43.2	32.5	14.2	89.9	10.1
	3.1	3.67	35.8	30.8	18.6	85.2	14.8
	7.0	3.77	36.2	31.8	18.5	86.5	13.5
	13.5	1.96	35.3	32.5	18.1	85.9	14.1
	26.4	3.22	35.9	32.3	20.5	88.7	11.3
	33.7	2.45	38.7	25.0	21.4	85.1	14.9
Boric Acid	0	1.04	43.2	32.5	14.2	89.9	10.1
	3.5	1.50	34.6	41.0	14.5	90.1	9.9
	7.7	1.75	30.8	44.3	15.2	90.3	9.7
	10.5	1.81	31.4	46.0	13.0	90.4	9.6
	13.0	1.92	27.1	48.3	15.8	91.2	8.8
Borax	0	1.04	43.2	32.5	14.2	89.9	10.1
	2.8	2.41	29.0	36.4	15.6	81.0	19.0
	5.4	2.17	34.6	33.7	16.3	84.6	15.4
	13.0	2.25	34.6	36.2	13.1	83.9	16.1
	20.3	2.10	36.2	37.0	12.4	85.6	14.4
	29.0	2.15	40.0	27.0	18.0	85.0	15.0
	34.5	2.29	34.9	29.8	19.5	84.2	15.8
Borax;	0	1.04	43.2	32.5	14.2	89.9	10.1
Boric Acid	2.6	2.03	39.5	33.5	16.9	89.9	10.1
7 : 3	4.6	2.50	37.9	33.9	18.0	89.8	10.2
	8.4	2.30	38.6	37.9	12.7	89.2	10.8
	16.5	2.45	39.2	33.8	16.4	89.4	10.6
	30.1	2.54	36.9	36.4	13.9	87.2	12.8
	43.7	2.35	42.3	33.5	12.1	87.9	12.1

somewhat with addition of the salts, but is apparently the same for all, irrespective of their flameproofing action. On this basis, there appears to be little if any justification for further consideration of the gas phase as being directly related to retardant action. However, the other volatile but readily condensable products, accumulated as tars, appear to be more closely related to non-flaming tendencies and are considered in detail in the following section.

2. LIQUID PHASE PRODUCTS

The aqueous distillate obtained from the pyrolysis or controlled combustion investigations contains the tarry primary dissociation products which appear to be critically related to the flaming characteristic of fabrics. In the borate retardant system, the agreement between the flame test data and the dry tar is particularly good. This system lends itself very readily to studies of this kind since the retardant does not contaminate

the distillates, which may be determined with considerable accuracy. precision with which this phase follows the inflammability of treated ton fabrics is demonstrated in Figure 20, where large reduction in amount is observed for mixtures of borax and boric acid when the components are in the ratio of 1:1 or 7:3. However, when the boric acid dominates in the system, as in the 3:7 mixture, the tar reduction is quite as great, which corresponds to the poorer flame-retarding quality of this blend. Moreover, the individual components alone on the fa

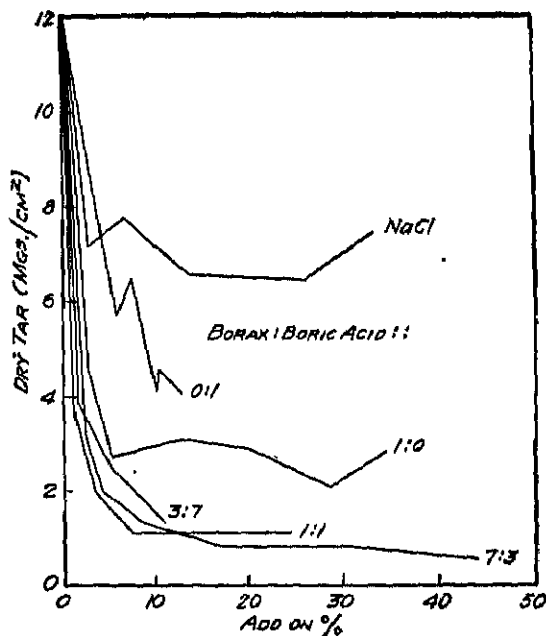


Figure 20. The reduction in the amount of volatile cellulose fragments as indicated by mixtures of borax and boric acid in comparison with that produced by sodium chloride

follow the order of their fair to poor efficiencies compared with the ineffective and ineffective sodium chloride. The relation between the tars and burning characteristics is summarized in Figure 21 for this system, where it seems that the production of these fragments must be reduced below 2 milligrams per square centimeter of fabric before flaming ceases in the vertical strip test immediately on removal of the flame source. This value appears to be rather critical, and increasing the tar yield from 2 to 4 milligrams per centimeter of fabric results in considerable flaming after the instigating source has been removed, although propagation of the flame may not proceed longer than 10 or 20 seconds. However, with the fuel supply greater than 4 milligrams, continuous burning proceeds until the fabric is completely consumed.

The total condensable distillates resulting from the combustion experiments contain considerable water. The aqueous portion is increased with the addition of salts to the fabric, while the tarry products are decreased

greatly for the addition of the effective retardants. The net result, as shown in Table 7, is not only a reduction in the amount of the tarry fuel supply but also a lowering of its effective concentration by dilution with water.

Although the supply, rate and concentration of these volatile fragments are altered radically by the effective retardants, their actual composition does not appear to be changed to any great extent. The tarry constituents contain hydroxyl, methylene, methyl, carbonyl, ethylene and ester groupings as determined by their infrared absorption spectra, which is in har-

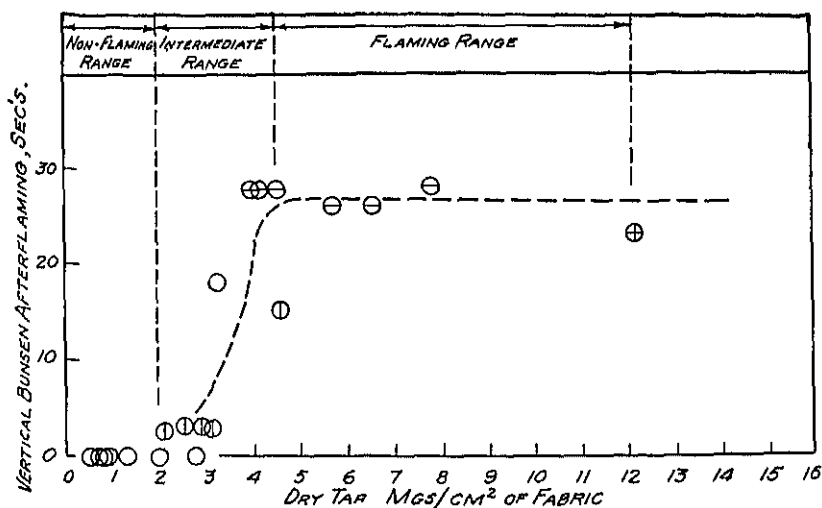


Figure 21. The correlation between the evolution of volatile fission products from cellulose and the flaming characteristics of fabrics.

⊕ untreated fabric, ⊖ treated with boric acid; ⊙ treated with borax, and ⊗ treated with borax and boric acid in the weight ratio of 7:3

mony with theoretical considerations regarding the probable course of the disintegration of the cellulose molecule. Moreover, the absorption curves of the tars from treated and untreated cotton show the same general absorption maxima and with nearly equal intensities

The analytical data suggest degradation nuclei of the pentose or furfural type, with composition not varying very widely with the amount of retardant or its type. As shown in Table 8, the carbon and hydrogen content of the various tars show no distinct variation with the effectiveness of the retardant, and although the products are highly reducing in nature their carbonyl content is not greatly changed by retardant additions.

Measurement of the relative inflammabilities of the tars from treated and untreated cotton indicates no great differences in the rates of flaming with different retardants. The conditions of burning fabric are readily

Table 7. The Variation of the Quantities of Liquid Phases Produced During the Controlled Combustion of Cotton Fabrics in the Presence of Various Materials

Retardant	Add-On %	Dry Tar mgs/cm ²	Aqueous Fraction mgs/cm ²	Tar in Distillate %	Yer After 50
Sodium Chloride	0	12.20	0.24	56.9	2
	3.1	7.05	14.31	33.0	2
	7.0	7.80	10.25	43.2	2
	13.5	6.50	13.88	31.0	2
	26.4	6.43	14.37	30.9	2
	33.7	7.43	14.02	34.8	2
Boric Acid	0	12.20	0.24	56.0	23
	3.5	7.80	15.90	33.1	23
	7.7	6.53	15.65	29.4	23
	10.5	4.52	15.03	23.1	23
	12.0	4.00	14.15	22.0	23
Borax	0	12.20	0.24	56.9	23
	2.8	4.55	4.70	27.9	15
	5.4	2.02	14.25	15.5	3
	12.0	3.03	15.90	16.2	3
	20.3	2.88	15.28	15.8	3
	29.0	2.08	14.05	12.4	3
Borax: Boric Acid 7 : 3	34.5	2.75	15.80	14.8	0
	0	12.20	0.24	56.9	23
	2.6	3.18	12.57	20.2	18
	4.6	1.97	13.20	12.9	0
	8.4	1.28	13.90	8.4	0
	16.4	0.85	12.48	6.4	0
	30.1	0.83	14.49	5.4	0
	43.7	0.55	10.10	5.2	0

Table 8. The Properties of the Tarry Distillation Products Isolated During the Controlled Combustion of Absorbent Cotton

Retardant	Add-On %	C %	H %	Reducing Power	Fraction of Tar Dissolved		
				Cu ₂ O gms/gm tar	Water	in % Acetone	Isopropa
Sodium Chloride	0	48.43	6.67	0.47	—	—	—
	1.1	51.66	6.35	0.43	—	—	—
	2.7	54.90	6.33	0.35	—	—	—
	7.0	53.51	6.47	0.40	—	—	—
	16.2	53.43	6.53	0.38	—	—	—
Boric Acid	0	48.43	6.67	0.47	13.6	45.5	36.8
	2.5	48.86	6.67	0.50	22.9	50.7	5.7
	3.5	49.17	6.18	0.50	16.1	45.7	23.8
	5.3	46.25	5.95	0.55	24.7	46.9	15.7
	7.3	42.10	6.37	0.49	40.2	43.6	26.1
	12.3	35.30	8.57	0.41	17.8	36.9	39.6
	21.6	25.60	7.83	0.42	23.2	29.0	34.6
Diammonium Phosphate	0	48.43	6.67	0.47	—	—	—
	2.3	51.01	5.58	0.53	—	—	—
	6.2	53.48	5.09	0.45	—	—	—
	10.0	50.11	5.44	0.34	—	—	—
Borax: Boric Acid 7 : 3	0	48.43	6.67	0.47	13.6	45.5	36.8
	1.5	45.50	6.51	0.51	21.2	42.1	33.1
	3.2	47.88	6.20	0.55	14.2	41.0	44.7
	6.1	49.85	5.98	0.50	17.8	37.8	25.6
	14.3	50.14	6.93	—	—	—	—

simulated by application of the tar in methanol to asbestos fabric, drying and then determining burning rates of strips of the material inclined at 45° to the horizontal. Results of this nature are given in Table 9, where it

Table 9. The Inflammability Characteristics of Tars Isolated During the Controlled Combustion of Various Celluloses

Source of Tar	Add-On of Tar mgs/cm ² of Asbestos	Burning Rate cms/sec.
Absorbent Cotton	32.4	0.081
	29.8	0.088
	27.4	0.096
	25.5	0.106
Absorbent Cotton + 9% Borax:Boric Acid (7:3)	26.1	0.082
	25.6	0.082
	22.4	0.081
	22.1	0.101
Absorbent Cotton + 10% Boric Acid	32.1	0.110
	22.3	0.106
	21.6	0.103
	19.1	0.125
Absorbent Cotton + 10% Diammonium Phosphate	25.2	0.075
	21.6	0.076
	20.9	0.083

appears that the flame rates vary somewhat in the range of 0.08 to 0.12 centimeters per second irrespective of their concentration from 20 to 30 milligrams per square centimeter of fabric, and although the propagation is somewhat lower for the effective borate and phosphate products, the difference is not sufficient to be a major factor in flameproofing effects. It is to be noted here that the tar concentrations are somewhat in excess of those normally generated at a burning fabric surface where it is usually about 10 to 15 milligrams per square centimeter of fabric.

The tarry products are only slightly volatile except at elevated temperatures, where they change their characteristics rapidly either by cracking or polymerization processes. They exhibit high solubility in methanol, lesser solubility in water, higher alcohols and ketones and low solubility in hydrocarbon solvents. On the basis of their fractional solubility in solvents of various polarities they may be separated into less homogeneous mixtures, but these fractions are similar in chemical behavior. Retardants appear to influence burning by limiting the quantity rather than significantly affecting the quality factors of this phase.

3. SOLID PHASE PRODUCTS

The solid decomposition products resulting from the pyrolysis or controlled combustion of fireproofed fabrics consist of a carbonaceous residue,

derived from the cellulose itself as well as the thermal remnants from the added retardant. The rate of fabric decomposition and the resultant char production may be followed in an approximate manner by a study of the total residue obtained at various time intervals via use of the equipment previously described in Figure 15. During the early stages of the controlled

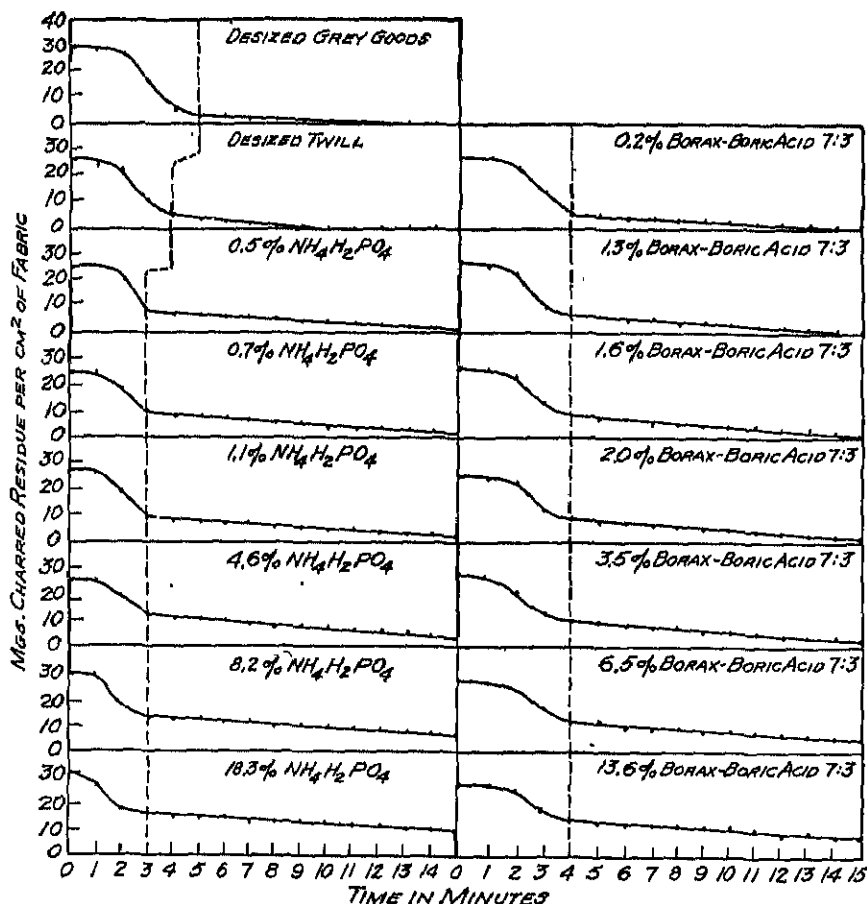


Figure 22. The effect of the phosphate and borate types of retardants on the rate of fabric disintegration during controlled combustion. (The per cent values are those added to desized twill.)

combustion, the fabric enters a short period of temperature elevation accompanied by only slight weight losses as shown in Figure 22. The duration of this induction period depends to a great extent upon the type of retardant as has been pointed out in an earlier section. However, once the fabric has reached a temperature above 300°C ., rapid deterioration proceeds with the evolution of tarry materials and a consequent rapid drop

in the yield of solid products. As seen in Figure 22, the second stage is again dependent upon the type of the retardant, the phosphate completing the rapid disintegration in less time than the borate type. On completion of the tar evolution a true char exists, whose further decomposition proceeds slowly via the oxidation of its carbon content to leave finally an ash of the added retardant. The over-all velocity of the latter oxidation reaction is quite uniform and independent of the amount or type of retardant as indicated by the similarity of slope in the linear sections of the curves of Figure 22.

This equality of char oxidation velocities is surprising since the two retardant types exhibit entirely different behavior in practical burning tests. The borate-treated fabrics show very pronounced tendencies to continue glowing after flame propagation has ceased, while the phosphate-treated ones suffer no flameless combustion. It would appear then that at least under these conditions the glowing of chars is not related directly to their over-all oxidation rates. However, the nature of this oxidation and the aspect of the charred residues is entirely different. The non-glowing materials shrink in dimensions with total retention of the original fabric structure, oxidation proceeding uniformly throughout the mass of the char. On the other hand, the glowing type of material as exemplified by the borate-treated fabric is oxidized very non-uniformly with partial to complete ashing of various locations in the char and non-retention of the original woven structure. The latter chars are coarse and brittle carbon masses which powder very readily while those from phosphate-treated fabrics are fine textured and relatively strong carbonized fibrous materials. The entirely different aspects of the chars from the various types of retardants are pictured in Figure 23. (*See facing page 55.*)

The various resistances to the glowing phenomenon are the most important property of the solid phase decomposition products of cellulose, and for a complete study a direct isolation of this reaction is required. The separation of the flaming from the glowing reaction is easily accomplished by first carrying out the disintegration in the absence of air. The system in Figure 24 is convenient, where either nitrogen or carbon dioxide enters a preheating section of the furnace at a required rate and passes over the fabric in the decomposition section. The fabric is maintained on the junction of a thermocouple which is inserted in a replaceable inner tube, the lower section of which collects the tarry products. After completion of the disintegration the fabric residue is raised to the upper section of the equipment, where it is cooled in an atmosphere of cold CO_2 from "dry-ice."

The fabric used in these experiments is an 8×5 cm. specimen rolled in the form of a cylinder. After the disintegration in the absence of air, its oxidizing properties may be studied by replacing the CO_2 with an air atmosphere or the char may be removed entirely from the furnace and

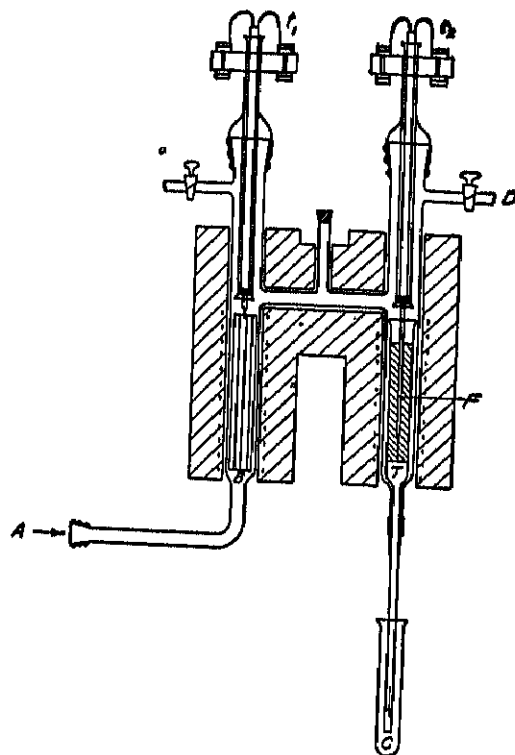


Figure 24. Equipment for thermal decomposition of fabrics in controlled atmosphere.

A: gas inlet; *B*: preheated section at temperature t_1 ; *C*: combustion tube; *F*: fabric at temperature t_2 ; *C*: gas exit; cooling gas inlet.

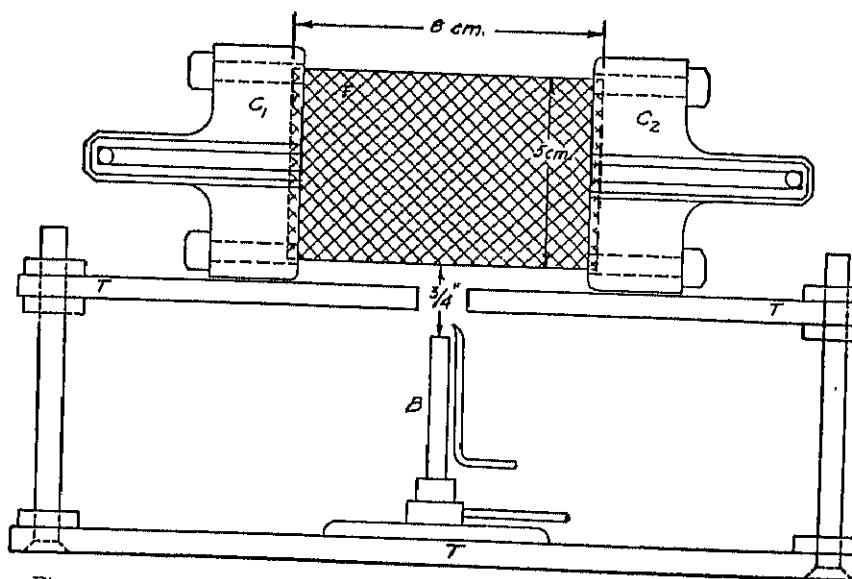


Figure 25. Equipment for determining the glowing characteristics of the charred residues from the thermal decomposition of treated fabrics. *B*: microburner with pilot light; *C*₁, *C*₂: paper clamps; *F*: charred fabric; *T*: transit stand.

subjected to a practical isolated glow test similar to that used in the regular Vertical flame testing procedures. The unrolled char is suspended between paper clamps over a microburner as shown in Figure 25. The flame is $1\frac{3}{4}$ inches in height and is just non-luminous. Its duration is 12 seconds, and the persistence of the flameless combustion is timed from the removal of the flame source until cessation of glowing. The extent of oxidation in this test is measured by the weight loss suffered due to con-

Table 10. Effect of Small Amounts of Retardants on the Extent and Duration of the Isolated Glowing Reaction of the Chars from Cotton Fabrics

Retardant	Add-On %	No. of Leachings	Initial Fabric Wt.	Loss During Pyrolysis mgs/cm ² of fabric	Loss Via Glow	Glowing Time sec.
Ammonium	0	0	26.90	21.40	5.08	73
Dihydrogen	0.05	0	24.36	18.40	2.40	78
Phosphate	0.1	0	24.50	19.58	2.74	70
	0.25	0	24.82	18.30	3.45	94
	0.5	0	24.66	16.99	0.77	9
	1.0	0	24.05	15.71	0.33	0
	15.0	0	33.30	17.20	0.07	0
	15.0	1	27.62	17.81	0.44	0
	15.0	2	26.31	20.05	0.65	27
	15.0	3	28.73	20.21	0.82	45
	15.0	4	28.10	23.26	4.14	210
	15.0	5	28.27	23.67	3.64	195
Commercial	0	0	26.90	21.40	5.08	73
Sulfamate:	0.05	0	25.77	20.94	3.47	90
Phosphate	0.1	0	25.98	20.61	4.02	120
Mixture	0.5	0	22.77	16.57	3.04	78
	1.0	0	24.87	16.94	0.78	20
	15.0	0	32.11	17.51	0.03	0
	15.0	1	28.67	19.14	1.12	0
	15.0	2	28.88	23.39	2.29	145
	15.0	3	27.38	22.54	3.81	240
	15.0	4	28.61	23.45	4.59	215
	15.0	5	28.07	22.75	4.09	185

tact with the flame source and the subsequent oxidation by the glowing reaction.

Preparation of chars from various fabrics at a nitrogen velocity of 400 cc. per minute and a temperature of 350° C. leads to the results of Table 10, wherein the effects of the phosphate and sulfamate mixture types of retardant are shown in comparison with the untreated fabric. It appears that very decided resistance to glow is imparted to cotton by the addition of small amounts of these materials, the phosphate being the most efficient. In the case of the phosphate, complete resistance to flameless combustion is obtained upon the addition of from 0.5 to 1.0% to the fabric, while continued addition seems to affect only the amount of oxidation ensuing in the presence of the flame source as indicated by the lower loss during

the glow test. The ease with which the inhibiting materials are removed on static leaching for 15 minutes in water is also demonstrated, but retardants being reduced presumably below the minimum requirement more than one mild water leaching process.

Similar experiments on a number of retardants and retardant mixtures are reported in Table 11. Here it appears that an inert and ineffective

Table 11. Effect of Large Amounts of Retardants on the Extent and Duration of Isolated Glowing Reaction of the Chars from Cotton Fabrics

Retardant	Add-On %	Initial Fabric Wt.	Loss During Pyrolysis mgm/cm ² of fabric	Loss Via Glow
None	0	26.90	21.40	5.08
Sodium Chloride	10	27.36	18.34	2.35
	20	30.06	18.51	2.04
Ammonium Sulfamate	10	27.92	15.07	10.55
	20	29.52	16.70	9.80
	10	27.42	16.47	7.51
Borax	30	30.71	16.96	7.66
	40	34.12	17.00	9.39
Boric Acid	10	24.76	13.50	0.39
	20	25.48	13.80	0.35
Ammonium Dihydrogen Phosphate	10	27.64	15.26	0.07
Borax: Boric Acid (3: 7)	10	28.37	14.07	0.32
Borax: Boric Acid (1: 1)	10	26.30	13.20	1.22
	20	28.52	13.26	0.28
	5	25.42	13.58	7.86
Borax: Boric Acid (7: 3)	10	26.08	13.64	5.67
	20	29.22	15.21	0.48
Borax: Boric Acid: Ammonium Dihydrogen Phosphate (1: 1: 2)	10	30.56	15.96	0.21
	20	30.73	13.15	0.20
Borax: Boric Acid: Ammonium Dihydrogen Phosphate (7: 3: 5)	10	29.75	15.18	0.21
	20	33.42	15.32	0.22

material such as sodium chloride has little if any effect on the isolated glowing reaction, while the sulfamate and borax appear to accentuate it. This is due, probably, to the larger amounts of char remaining after the disintegration reaction. However, with the phosphate and boric acid, the extent and duration of this reaction are reduced to very low values, the former being the most efficient in respect to oxidation in the presence of the flame source. With mixtures of borax and boric acid, the glowing retarding component loses its inhibiting effect if the borax component is in excess. In the three-component system, which includes the very effi-

phosphate, glow propagation is also reduced to nil although even here the borax appears to exhibit a deleterious action in that the oxidation in the presence of the flame is considerably greater than that obtained with phosphate alone on the char.

These effects indicate the composite nature of the secondary oxidation of the charred residues from fabrics and point to changes in the course rather than to the over-all rate or extent of the reaction as being the important effect brought about by retardants. Preliminary experimentation establishes that the afterglow phenomenon is a general one for carbon

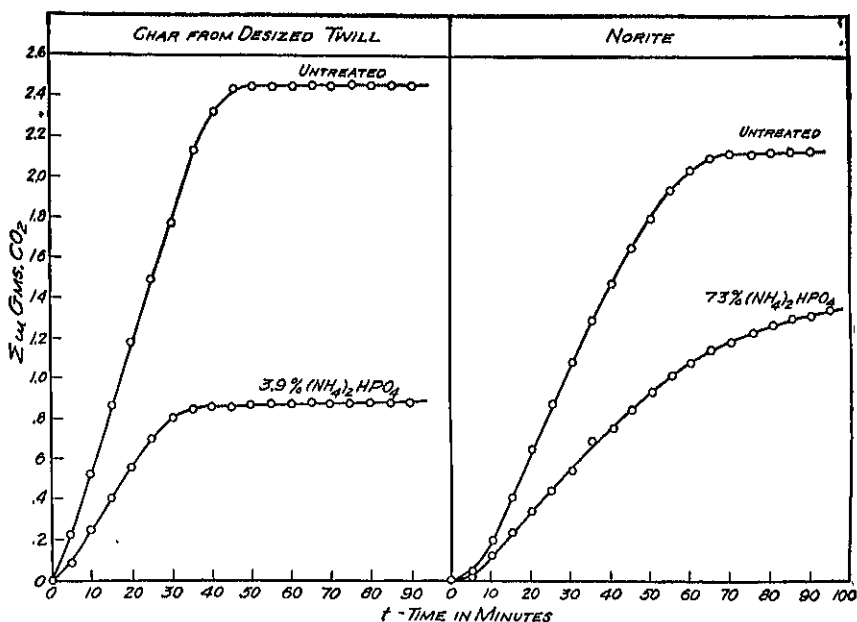


Figure 26. The similarity in the oxidation characteristics of charred residues from fabrics and absorbent carbon as influenced by glow-retarding phosphates

and not confined to fabric residues. This is shown quite readily in Figure 26, where the rate of CO₂ evolution is determined both for fabric residues and for Norite absorbent carbon. In each case both the rate and extent of this oxidation is reduced for the addition of ammonium phosphate when oxidation is carried out under identical conditions in a standard "Combustion Train." The standardized combustion conditions of one gram of char at 500° C. and 200 cc. of air per minute arise from an examination of the factors affecting the oxidation reaction for untreated absorbent carbon. Here it is found that with variation of the temperatures above 300° C. both the rate and the extent of the oxidation to CO₂ increase with increased temperature, but above 600° C. the rate is insensitive to the temperature, while the extent of the reaction continues to increase until

at somewhat above 700° C. the theoretical production of CO_2 is approached. Similarly, variations of air supply influence the reaction, greater velocities promoting a more rapid reaction. In the vicinity of 200 cc. of air per minute, increased air supply does not influence either the rate or extent of CO_2 evolution, which are here solely dependent upon the temperature and amount of carbon present. Further examination shows that with variation of the carbon concentration from 0.25 to 1.0 gms., little if any change in the CO_2 rate occurs, while the total amount generated is directly proportional to the original carbon charge. The chosen conditions of 500° C. and 200 cc. of air per minute per gram of carbon are hence considered ideal for comparative studies of this kind.

For thorough studies on the kinetics of the oxidation of charred fabric residues, the equipment of Figure 27 provides a rapid and convenient

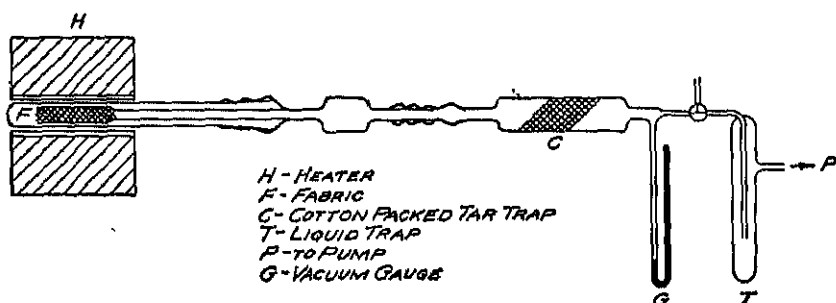


Figure 27. Pyrolytic equipment for the production of charred residues from fabrics for further oxidative studies.

means for producing chars from variously treated materials. Here the fabric is decomposed under pyrolysis conditions of 500° C. and less than 5 mm. Hg. absolute pressure for various periods of time. On cooling, the residual char is removed and one gram is inserted on the thermocouple junction of the equipment shown in Figure 28. Dry and CO_2 -free air at 200 cc. per minute passes over the char where the initiating temperature is 500° C. The carbon dioxide evolution is determined at various time intervals at the absorbent system C_1 and C_2 while the residual CO is further oxidized by passage over hot copper oxide and is determined at time intervals by absorption at C_4 and C_6 .

In the oxidation of the char, the course and rate of the various reactions appear to be dependent not only on the retardant but also upon the completeness of the pyrolysis. Higher temperatures and pyrolysis times provide for more complete tar generation and give better differentiation for the course of the oxidation of chars from treated and untreated fabrics. These effects are shown in Figure 29, where a fabric containing 5% of diammonium phosphate is compared with the original untreated cotton.

The phosphate apparently changes the course of the oxidation, favoring the production of CO rather than CO_2 , and the effect is most apparent for

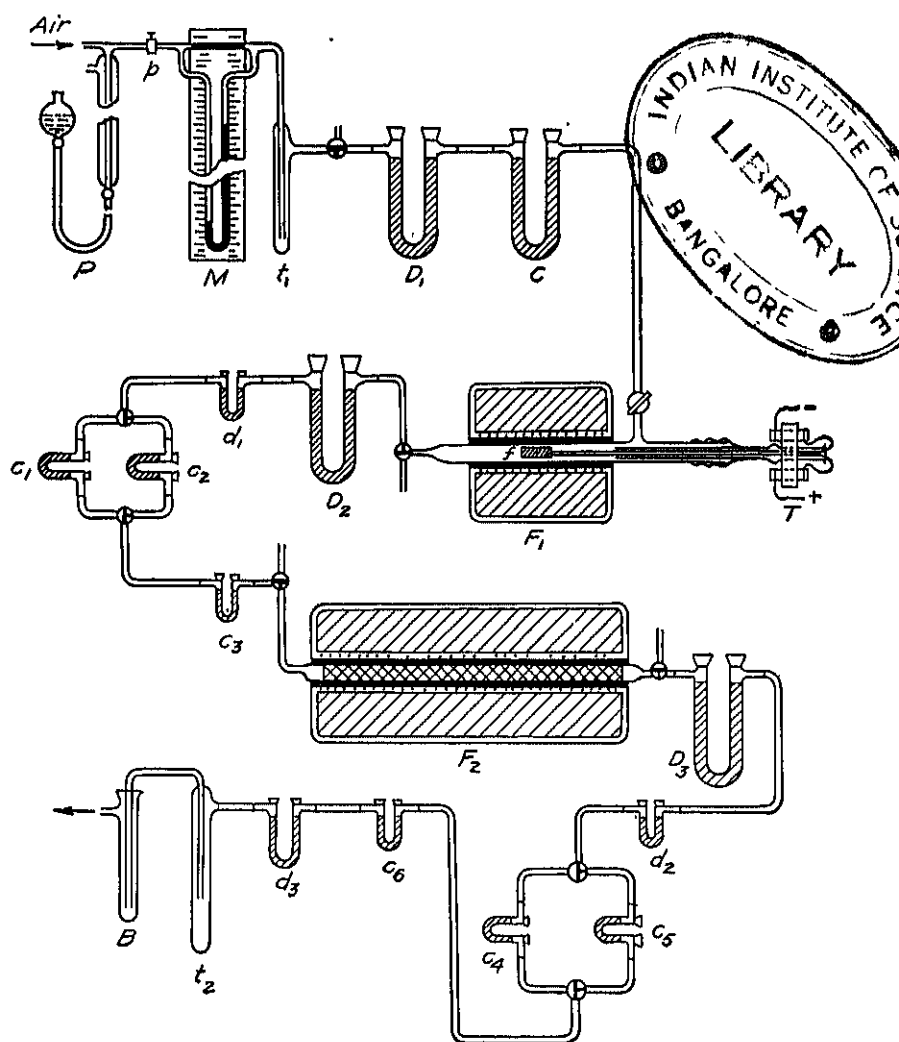


Figure 28. Equipment for kinetic studies on the oxidation of charred residues from fabrics

P, M, t₁: air inlet system; *D₁, C*: purification of inlet air; *F₁, f, T*: oxidative system for char; *D₂, D₁, C₁, C₂, C₃*: CO_2 determination system; *F₂*: CO oxidation system; *D₃, d₃, C₄, C₅, C₆*: CO determination system; *d₂, t₂, B*: gas exit system

chars prepared by lengthy pyrolysis. Similar effects are shown for pyrolysis at 550°C . in Figure 30, where the promotion of CO formation is even more apparent with increased completeness of pyrolysis.

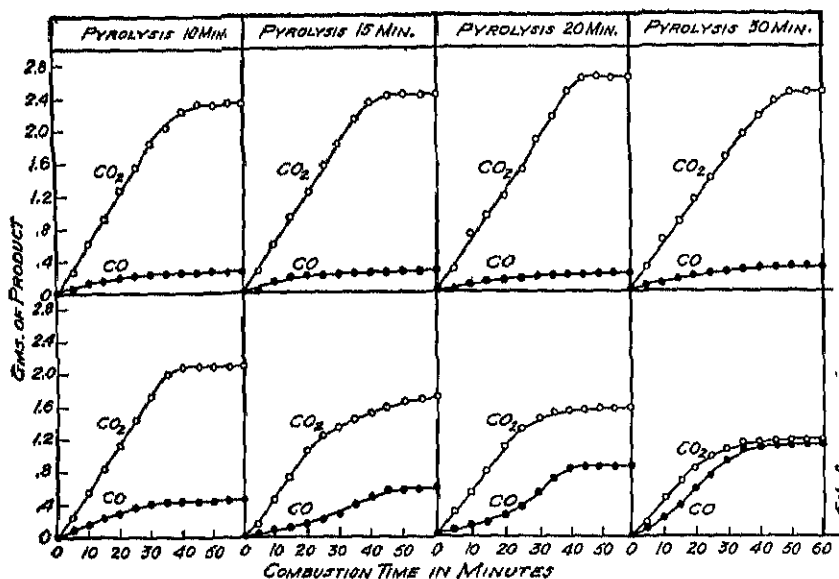


Figure 29. Comparative data for untreated fabric and that treated with 5% diammonium phosphate, showing the influence of the retardant in altering the course of the oxidation of the charred residues from these fabrics.

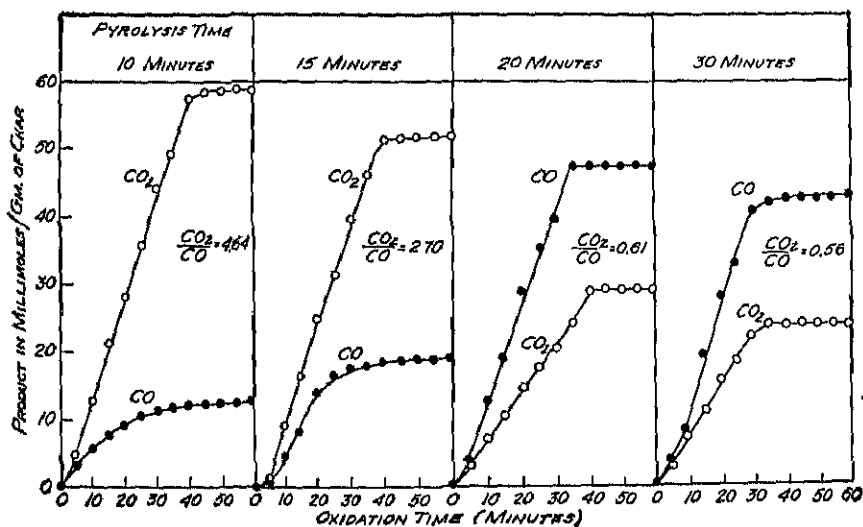


Figure 30. The influence of 4% diammonium phosphate in promoting the oxidation of charred residues from fabrics in the direction of CO rather than CO_2 ; a function of the completeness of the preliminary pyrolysis to eliminate the tarry products responsible for flaming.

The agreement between the course of char oxidation and the tendency for flameless combustion is demonstrated in Figure 31. Here the very efficient phosphate glow retardant reduces the CO_2 evolution from 2.5 to 0.8 grams per gram of char for additions as low as 1% of the retardant to the fabric, and this reduction is not affected appreciably by further additions of the phosphate. Similar effects are obtained for the fairly effective boric acid where again the CO_2 evolution is reduced, but not to the extent of that obtained for the phosphate, the minimum value being about 1.2 grams of CO_2 per gram of char irrespective of the amount of boric acid added originally to the fabric. However, with a glowing type of retardant such as borax, small additions have little if any effect on the course of the oxidation of the resultant char, and even for higher amounts the value never falls below 2.0 grams of CO_2 per gram of char. These results are in direct accord with the observed facts that quantities of ammonium phosphate or boric acid as low as 1% will prevent glow propagation but that borax although inhibiting flame propagation will not prevent the travel of flameless combustion in a fabric, irrespective of the amount of the retardant. The prime difference apparently lies in the relative abilities of these retardants to promote the oxidation of charred fabric residues to the monoxide rather than the dioxide state of carbon.

Charred residues obtained from the pyrolysis of glowproofed fabrics retain their non-glowing characteristics even after 14 hours' extraction with hot water in a modified Soxhlet apparatus. Further extraction for 5 hours with methanol, refluxing for 1 hour with 0.1 N. NaOH and 14 hours' additional water extraction have no further effect on an originally glowproofed char. This resistance is exhibited by the phosphate- and boric acid-treated materials and their blends with borax. Apparently the borax component is removed quite readily by the extraction, leaving the glowproofing agent alone on the char.

Chars from untreated cotton fabric and those from material treated with borax glow very readily, but when these chars are unpregnated with either boric acid or diammonium phosphate the glowing tendency is greatly reduced. These investigations indicate that the physical form or state of the carbon is not a governing factor, since chars of the glowing type may be converted to the non-glowing type by simple addition of the anti-glow agent.

The tenacity with which $(\text{NH}_4)_2\text{HPO}_4$ is retained after pyrolysis is dependent to some extent upon the presence of other materials in the charred residue. Mixtures of glow retardants with borax are not retained nearly so well as is the anti-glow reagent alone, while borax alone is removed very quickly by extraction. The analyses of the charred residues both before and after extraction show that practically all the originally added phosphate is retained by the char as demonstrated by Table 12, and its retention appears to be independent of the extent of the pyrolysis. However,

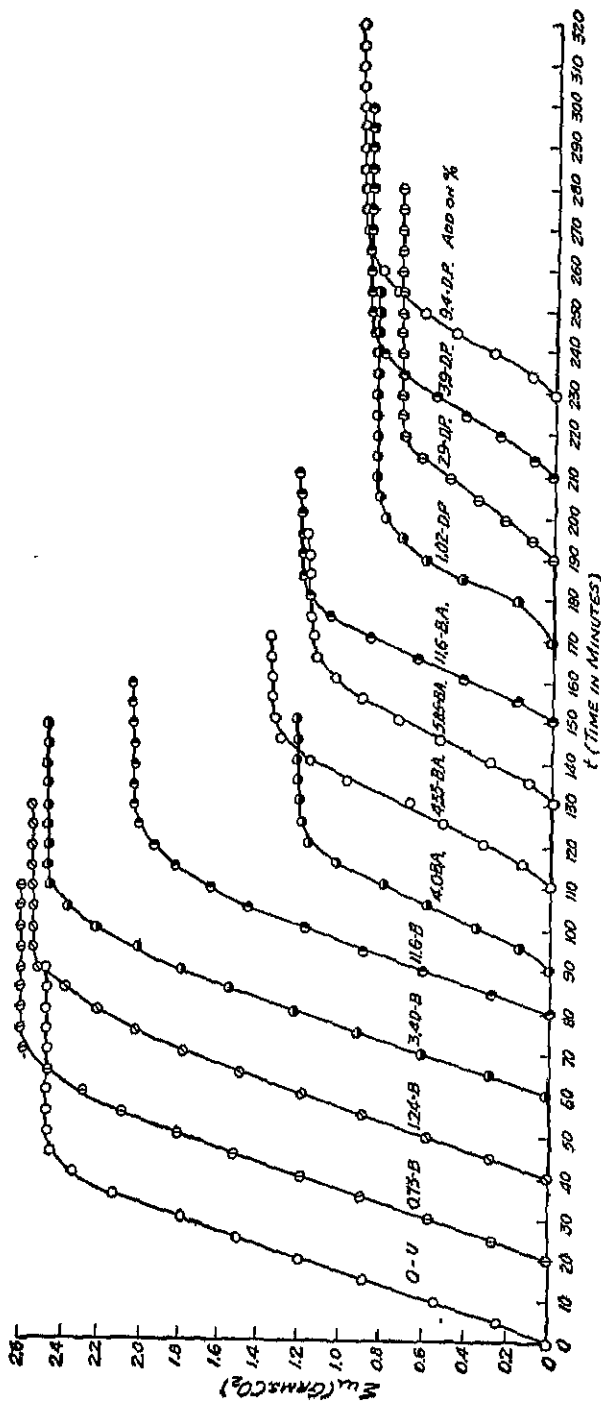


Figure 31. The effect of various retardants on the evolution of carbon dioxide during the oxidation of the charred residues from cotton fabrics.

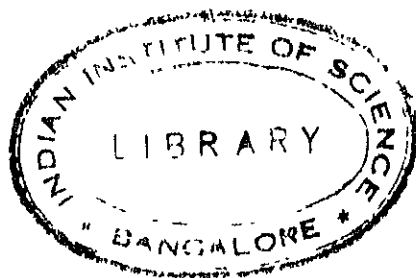
Chars from—U: untreated fabric; B: borax treated; B.A.: boric acid treated; and D.P.: diammonium phosphate treated fabric. The per cent values are those added originally to the desired twill.

Table 12. Composition of the Pyrolytic Chars from Various Fabrics

	Theory ($C_{11}H_{10}O_4$)	Untreated	5% $(NH_4)_2HPO_4$		5% Borax	
			Before Extraction	After Extraction	Before Extraction	After Extraction
C %	44.4	85.28	78.05	79.14	77.38	87.33
H %	6.2	3.40	3.04	3.49	3.19	3.98
Ash %	0	3.60	2.99	3.57	9.29	0.76
H_3PO_4 %	0	0	0.95	7.7	0	0
H_2O Soluble	0	0.1	- 1.4	0	15.9	0

mixture of the phosphate with borax lowers the H_3PO_4 retention somewhat, probably due to the Na_3PO_4 formation.

X-ray diffraction patterns of the fabrics, both before and after pyrolysis and extraction, indicate that at most the retention of the glow retardant is due to a surface intermicellar reaction. The patterns for the treated fabrics are identical with those from cellulose and the patterns obtained from the pyrolyzed and extracted chars are consistent with those from carbon.





Chapter III

Mechanisms of Flameproofing

S. Coppick

Although the literature on the subject of flameproofing is quite extensive, the majority of the experiments performed have been of a practical nature dealing with the development of new and improved flame-retarding materials and methods of application. For this reason, there is little fundamental data available pertaining to the fundamentals of flameproofing agents and the mechanisms by which they function. In the absence of supporting data, there has been in the past considerable speculation concerning these mechanisms and, as a result, several different explanations of the phenomenon of flame retardation have been proposed. In contrast, the phenomenon of afterglow has only in recent years been recognized as an independent corollary of afterflaming and hence has not been the subject of such extensive speculation. In further advances into the field of flameproofing, it is highly desirable that future experiments be based, not on theoretical speculations, but rather upon fundamental mechanisms which have some foundation in fact.

In the preceding chapter, flame-retarding materials were shown to exert a specific influence upon the rate and extent of formation of the degradation products of cellulose. This influence may be regarded as the primary effect of flameproofing action. It would be well, therefore, to delve further into the fundamental mechanisms in an attempt to uncover the basic causes of these primary effects. Consequently, the following chapter has been devoted to consideration of the mechanisms of the prevention of afterflame and afterglow. An attempt has been made to discuss these mechanisms as advanced, placing proper emphasis upon those which appear to have a better foundation in experimental fact. It is quite apparent that considerable additional experimentation is called for on these fundamental aspects of flameproofing.

A. PREVENTION OF AFTERFLAMING

1. CHEMICAL THEORIES

An examination of the composition of the efficient fire-retarding materials reveals that with only a few exceptions they include those materials

which might be expected to enhance the decomposition of cellulose under the influence of heat. Moreover, the majority of retardants have an appreciable degrading action on cellulose even at normal or slightly elevated temperature or when subjected to sunlight. At first this would appear to be contrary to their retarding action in the presence of a flame, but it is to be remembered that flameproofing does not involve protection from damage to that area in the vicinity of the heat source, but simply excludes propagation of the flaming reaction.

The most common agents which have a pronounced degrading action on cellulose are the strong alkalies, the mineral acids and oxidizing agents as shown in Chapter II, and it appears to be more than a coincidence that these should be the materials most effective as fire retardants. It is not necessary that these degrading chemicals be used directly due to their pronounced tendering effects under atmospheric conditions, but a more practical method is to provide such combinations that will produce the active ingredient under the influence of heat from the flame source. On this basis the theory has been proposed that the flame-retarding effects shown by many substances are due to their promoting the breakdown of the cellulose at high temperature in a direction other than that which takes place in their absence.

The substances which produce strong alkali at high temperatures include the alkali salts of weak acids, *i.e.*, borax, sodium carbonate and bicarbonate, sodium tungstate, silicate, stannate, molybdate, aluminate, and arsenate. None of the neutral salts of strong acids and bases are subject to marked decomposition at flame temperatures and to produce strong acids, the salt with a weak base is preferred. Those most easily decomposed are the ammonium salts and include the phosphates, sulfamate, sulfate and halides, although calcium, magnesium and zinc chloride are relatively unstable and have a pronounced flame-retarding effect. The easily reducible oxides are well known in their degrading action on cellulose and may be used directly or in the hydroxide or hydrated form which include ferric, stannic, arsenic, chromic and titanio. The standard oxidants and oxidation promoters such as potassium nitrate, the metallic chromates, selenium, potassium permanganate and thiocyanate are also fairly effective retardants ¹

Evidence in favor of this theory is given by Ramsbottom and Snoad ¹ who limited their intensive investigations to the borax-boric acid system, and by Metz, ² Serebrennikov, ³ Palmer, ⁴ and Richardson ⁵ in their studies

¹ Ramsbottom, J. E., and Snoad, A. W., Dept. of Scientific and Industrial Research, Great Britain, Second Report of the Fabrics Co-ordinating Research Committee (1930)

² Metz, L., *Gasschutz U Luftschutz*, 6, 260 (1936)

³ Serebrennikov, P. P., U. S. Forest Service Div of Silvics, Translation, 9, 151 (1934).

⁴ Palmer, R. W., *Ind. Eng Chem*, 10, 264 (1918).

⁵ Richardson, N. A., *J. Soc. Chem. Ind.*, 56, 202 (1937).

on the fireproofing of woody materials. The data indicate that the effective chemicals alter the course of cellulosic decomposition favoring the formation of lesser amounts of inflammable tars and gases and increasing the production of non-volatile carbonaceous material. The theory is also in direct accord with the effects shown in the pyrolysis and controlled combustion studies of Chapter II, wherein marked decreases in both the amount and concentration of the available tarry fuel supply are observed on the addition of the retarding chemical, and this fraction is directly related to the flaming characteristics of the fabric.

A schematic summary of the change in the course of cellulosic fission brought about by retardants is given in Figure 1. Here the normal reaction

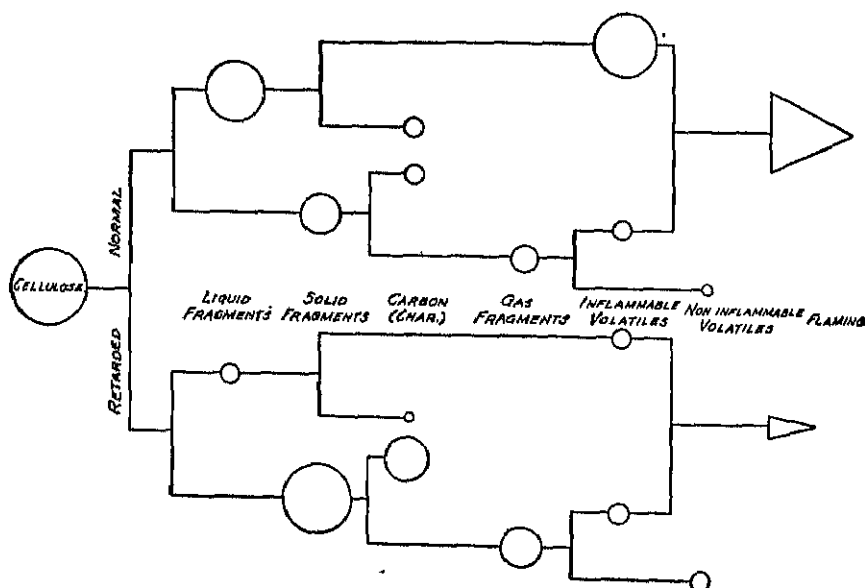
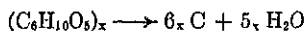


Figure 1. Schematic representations for the path of the thermal degradation of cellulose in the presence and absence of retardants, and the relation to the flaming characteristics. The size of the spheres represents approximate quantities of the various fission products.

is pictured as proceeding initially to give large quantities of volatile and relatively low molecular weight fragments which are easily cracked and oxidized in the vapor phase and constitute the flaming interface. The small amount of non-volatile charred residue is further decomposed to give minor amounts of gas and carbon, the latter being susceptible to oxidation by the flameless combustion reaction. In the presence of the directing influence of retardants, however, the course of the reaction appears to be toward fission of fragments of much greater molecular magnitude or of such structure to promote lesser volatility. The small amount of low

molecular weight tars pass off as before but their quantity is insufficient to support a continuance of the flaming interface. The non-volatile constituents are cracked in a solid phase reaction giving rise to larger amounts of gases and carbon than in the normal reaction. It appears that the critical reaction is the highly exothermic oxidative cracking of the degradation fragments, and it is essential that this process be confined to the solid phase if flaming is to be eliminated. The function of the retardant will then be to promote the initial breakdown in the direction of non-volatile fragments either by changing their relative size, molecular complexity or the nature of their side groupings. Any process such as cyclization, polymerization, polycondensation, or cross-bridging of these fragments should be effective in promoting their retention of the solid phase at high temperatures.

One of the specific mechanisms for the preferred course of cellulosic decomposition in the presence of a retardant would be the ideal where the whole of the carbon content would be confined to the solid phase. This involves a catalytic dehydration process such that the following prevails:



All fragments are thus confined to non-volatile carbon, and flaming cannot ensue. This mechanism has been proposed by Leatherman⁶ to explain the retardant action of metallic oxides, particularly the hydrated stannic oxide as originally used in the Perkin⁷ process. Similar catalytic pyrogenic decomposition functions are forwarded to explain the action of ferric, manganese, cobalt, antimony, lead, arsenic and zinc oxides, and are compatible with their known dehydrative activity in other reactions. The theory has been extended to cover a large number of the soluble inorganic salts which decompose at flame temperatures to produce desiccant materials such as NaOH, H₂SO₄, H₃PO₄, NH₂HSO₃, etc., and is substantiated by Leatherman's⁶ studies where heating of untreated fabrics and those treated with metallic oxides is conducted in a stream of air. Considerably more carbon is set free in the case of the treated fabrics, and in similar rapid heating experiments the water liberated from treated fabric is equivalent to about twice that normally produced from the untreated material. These results are in agreement with those of the combustion and pyrolysis studies described in Chapter II; however, the variation of the amount of water liberated with the quantity of added retardant is not quite sufficient to be accepted as conclusive evidence for the wide adaptability of the mechanism.

Another fundamental mechanism of wider applicability is that stimu-

⁶ Leatherman, M., U. S. Dept. of Agriculture, Circ. No. 466 (March, 1938).

⁷ Perkin, W. H., 8th Internat'l. Cong. Appl. Chem., Washington and New York, 28: 119-134 (1912).

lated by the observation of Sisson⁸ that the majority of the effective flame-retarding chemicals contain groupings which are active in hydrogen-bridging processes. The well-ordered and relatively inactive portion of cellulose is considered to involve the hydrogen bonding between adjacent hydroxyls, while the disordered and active portions are characterized by the bridging of adjacent chains via water molecules.^{9, 10, 11} The thermal stability of the system is critically related to these intermolecular linkages and it is proposed that upon contact with high temperature sources the bridging media are lost due to the thermal activity of water at these temperatures, but that the linkage may be maintained if a non-volatile component of sufficient hydrogen-bonding activity is present. The electronic configurations which promote strong linkages of this type in the cellulose system are $=O$, $-OH$ and $-NH_2$. These groupings are particularly prevalent in the more efficient retardants such as the phosphates, sulfates and sulfamates, and the theory proposes that thermal stability and the confining of fragments to the solid phase is due to a great extent to the hydrogen-bonding capacity of these compounds. It is further pointed out that the main chemical characteristic of the strong deliquescent salts and the hydrated salts effective in retardant action is their high hydrogen-bonding power, and although they prefer to stabilize their electronic configuration by bonding with water, in the absence of the latter the cellulosic hydroxyl serves the same function.

It has been observed in many instances that the thermal stability of the cellulose chain as a whole is intimately associated with the activity of the alcoholic groups. Thus, fission of the glucosidic linkages by the hydrolytic or oxidative process takes place much less readily if the hydroxyls are inactivated by substitution as exemplified by the relative stability of cellulose derivatives. The acidic retardants may then function not only on their capacity for side group inactivation by hydrogen bonding but also on direct substitution at flame temperatures. The bi- and tri-functional phosphates, sulfates, and sulfamates also provides for cross-linking through primary bonds to create further difficulties in the splitting of volatile chain fragments. This three-dimensional effect may proceed either via polymerization or condensation of aldehydic groupings as catalyzed by the strong acid or alkali thermal dissociation product of the retardant.

2. COATING THEORIES

As early as 1820, attention was called to the fact that among the known flame-retarding salts there exists a group which have a low melting point.

⁸ Sisson, W. A., Amer. Viscose Corp., discussions with the writer.

⁹ Huggins, M., *J. Org. Chem.*, 1, 407 (1936).

¹⁰ Heuser, E., "The Chemistry of Cellulose," John Wiley and Sons, New York (1944).

¹¹ Mark, H., *Chem. Revs.*, 26, 169, 181 (1940).

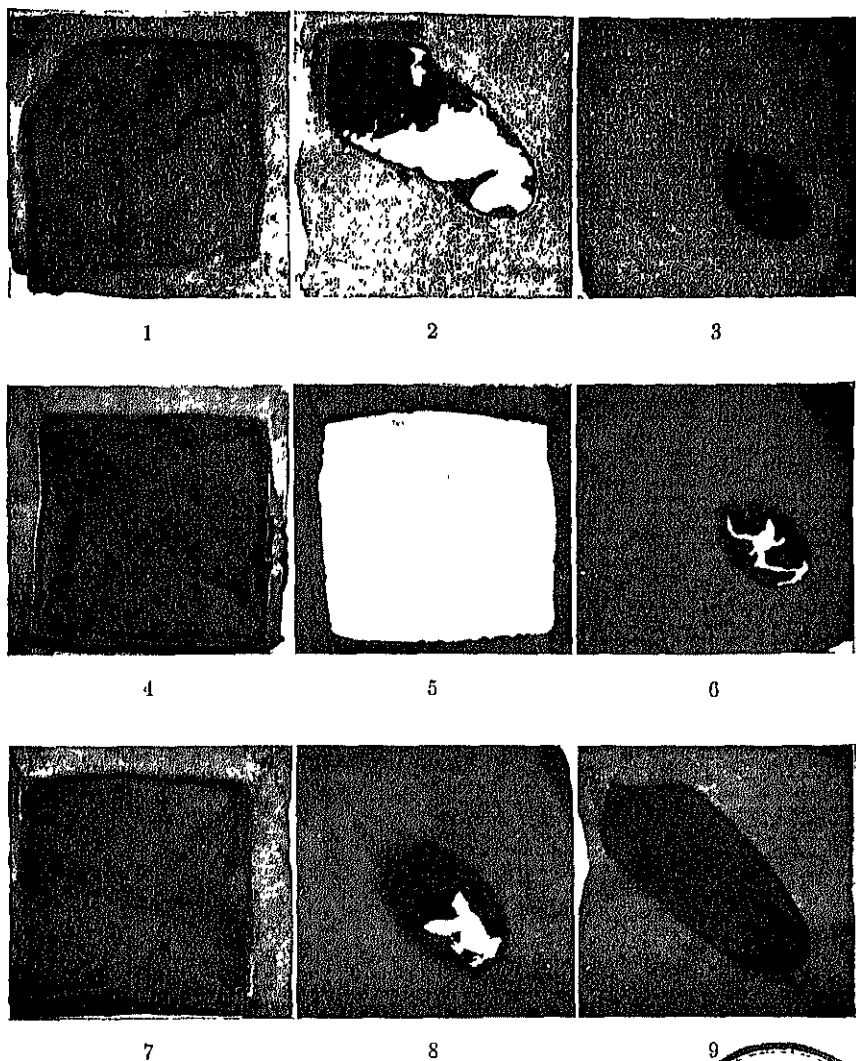
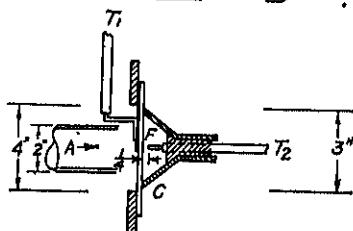
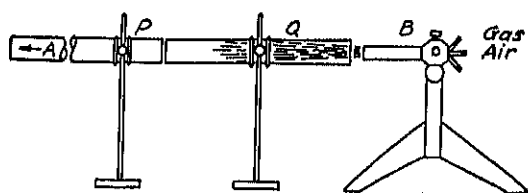


Figure 2. 45°-Microbunner flame test specimens.

1. 9% Boric acid (H_3BO_3)
2. 16% Borax ($Na_2B_4O_7 \cdot 10H_2O$)
3. 13% Borax:Boric acid (1:1)
4. 9% Boric acid (H_3BO_3)
5. 9% Trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$)
6. 10% Trisodium phosphate:Boric acid (1:1)
7. 9% Boric acid (H_3BO_3)
8. 9% Aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$)
9. 12% Aluminum sulfate:Boric acid (1:1)





B: burner; *Q*: quartz tube,
P: pyrex tube; *F*: fabric;
C: funnel; *Δ*: flame direction;
 T_1, T_2 : thermocouples,

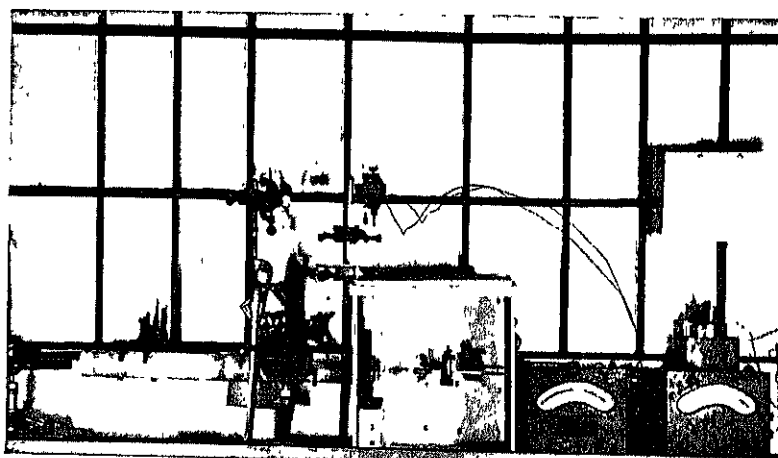
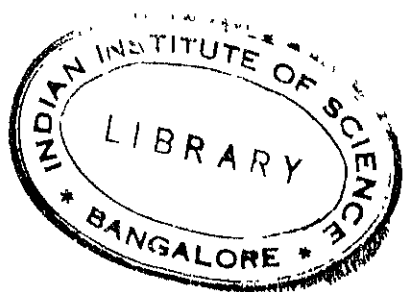


Figure 6. Equipment for studies of the insulation value of glowproofed fabric



point and upon contact with a flame fuse to cover the fabric with a glassy layer. Upon this Gay-Lussac¹² advanced the postulation that one of the mechanisms for flameproofing action involves the coating of cellulose with a non-penetrable skin whereby oxygen exclusion functions to prevent propagation of the combustion reaction. Various modifications of the original hypothesis have been forwarded, and the theory is very prevalent in recent literature.

The action of the borates has been explained on this basis and the theory is particularly suitable for considerations regarding the specific and anomalous behavior of the efficient mixtures of borax and boric acid. In researches conducted by the British Air Ministry,¹ this flameproofing system was investigated with considerable thoroughness, and it is pointed out that although each of the components alone performs a coating function, the mixture acts much more efficiently. Both borax and boric acid leave a badly distributed and poorly adhering crystalline deposit on a fabric, while the mixture has very little crystallizing tendency and on evaporation of the water leaves a glassy matrix which forms a tightly adhering and almost invisible covering over the cotton fibers. Charring tests indicate that this two-component layer is more impervious to air than are its constituents alone.

Heretofore, attention has been directed to the desirability for the formation of a vitreous layer or skin on the fiber surface; however, it appears that the most effective coating is one of less glassy nature. Investigations with mixtures of various salts show that there are wide variations in the respective abilities of certain blends to form frothy products when subjected to heat sources of an intensity comparable to flame temperatures. Moreover, the effectiveness of these mixtures of inorganic compounds in preventing afterflaming is somewhat proportional to their tendencies to form stable foams. The superiority of specific mixtures over the simple components is demonstrated in the 45° flame test specimens of Figure 2. The function of the foam appears to be not only to provide protection of the fabric from the air, but also serves as a barrier to the flame and entraps the volatile tars evolved during combustion.

The simple formation of a foam is not the only requirement for efficient flameproofing, although in general the agreement is rather good. For maximum retardant efficiency it is postulated that a two- or three-component system should have such properties that one component at least must decompose at a relatively low temperature with the evolution of large amounts of gaseous products. The decomposition temperature should be in the vicinity of 80 to 200° C. and the resulting gas phase of course must be non-flammable, i.e., either H_2O , CO_2 , NH_3 or SO_2 , etc. One of the other components must melt at a temperature near that at

¹² Gay-Lussac, *Ann. Chim. Phys.*, 18 (1823).

which gas evolution begins, and the mixture should be compatible with a uniform flux which solidifies as decomposition progresses. The foam resulting from these series of phase transitions should be a network-like structure stable at temperatures in the vicinity of 500° C.

The number of inorganic materials which have the desired properties is rather limited, and usually not all of the requirements are met. However, a pronounced foaming tendency usually leads to effective retardation although the relative efficiencies may not always follow the order due to improper foam structure as shown in Table 1. Here the flame height is reported as that attained when 5 grams of the retardant is heated in a test tube of 1-inch diameter for 5 minutes at 450 to 500° C.

It should be pointed out that this mechanism is not intended to describe the processes which lead to the effective action of the strong acid phosphate retardant. Here, undoubtedly, the prime cause for flameproofing is entirely different since foaming tendencies for the ammonium phosphate sulfamate and bromide are negligible.

3. GAS THEORIES

The hypothesis presumes that flameproofing may be accomplished by the impregnation of fabrics with a material which will decompose at elevated temperatures with the evolution of inert or difficultly combustible gases or vapors. Changes in the atmosphere in the vicinity of the fabric are supposed to serve either of two functions: the dilution of the flammable gases produced during normal cellulosic decomposition and the blanketing effect to exclude or reduce the prevailing oxidizing atmosphere of the environment. The supposition of a quenching action by rapid gas evolution is also prevalent in the general concept for mechanisms of this type. The effect of such changes in the concentration of gaseous fuel in air is presumed to raise the kindling temperature of the vapor mixture to such an extent that the rate of combustion is reduced, and in the limit it becomes zero, at which point flame propagation ceases.

Among the gases most commonly considered effective are: CO_2 , HCl , H_2O , and SO_2 . The theory is hence supported by the flameproofing action of sodium carbonate and bicarbonate, the ammonium halides, phosphates and sulphates, the chlorides of zinc, calcium and magnesium, hydrated salts such as borax and aluminum sulphate, and by ammonium sulfamate.

The relative efficiencies of the flame retardants which might function in this mechanism should depend upon several factors. The available gas supply, the decomposition temperature and the rate of gas evolution in the required temperature range should be the determinants. It is generally conceded that rapid gas evolution should proceed from the retardant at temperatures in the vicinity of that at which the cellulose

Table 1. Correlation Between Foaming Tendency and Flame Retardancy

Relative Efficiency Based Upon the Volume of Foam Formed (Ht. of Foam in 1" diam Tube)		Relative Efficiency Based Upon Performance in the 45° Microburner Flame Test	
Flame Retardant	Foam Ht. in.	Flame Retardant	After- Burne sec.
1 Boric Acid : Ammonium Dihydrogen Phosphate (1:1)	4.50	1 Boric Acid : Ammonium Dihydrogen Phosphate (1:1)	Char Area in. ² 15.0 1.44
2 Borax : Boric Acid (1:1)	3.50	2 Borax : Boric Acid (1:1)	7.7 1.67
3 Sodium Phosphate : Boric Acid (1:1)	3.50	4 Borax : Boric Acid : Diammonium Phosphate (7:3:5)	9.5 1.90
4 Borax : Boric Acid : Diammonium Phosphate (7:3:5)	3.25	3 Sodium Phosphate : Boric Acid (1:1)	10.5 2.06
5 Borax : Boric Acid (7:3)	3.25	6 Commercial Borate Mixture	8.4 2.08
6 Commercial Borate Mixture	2.75	5 Borax : Boric Acid (7:3)	9.5 2.19
7 Borax : Boric Acid : Diammonium Phosphate (1:1 2)	2.75	8 Borax : Diammonium Phosphate (1:1)	7.9 2.84
8 Borax : Diammonium Phosphate (1:1)	2.50	7 Borax : Boric Acid : Diammonium Phosphate (1:1:2)	8.8 2.86
9 Borax	2.75	10 Aluminum Sulfate	8.8 4.59
10 Aluminum Sulfate	2.00	9 Borax	15.8 Burned to end
11 Boric Acid	.25	11 Boric Acid	9.3 Completely burned
			70

decomposes, and a rough estimate places this at about 300° C. for maximum efficiency. Hence, the relatively low temperatures required for the decomposition of the ammonium salts, bicarbonates and hydrates are in favor of good performance.

It has been pointed out¹³ that although HCl would satisfy all the requirements in a mechanism of this type, the compounds which show an spontaneity for evolution of this gas, in the required temperature range usually decompose at appreciable rates either thermally or by hydrolysis under normal atmospheric conditions. Hence, their tendering effect on cellulose renders them of little if any practical importance. Furthermore, if more stable HCl donors such as the chlorinated resins are used, the gas evolution does not proceed at a sufficient rate until temperatures greatly in excess of 300° C. are reached, and they do not provide adequate flameproofing when used alone. However, in the presence of a dechlorination catalyst the velocity of gas evolution might be increased at the desired temperatures. This is cited as a contributing mechanism for the protection afforded by certain chlorinated materials in the presence of zinc oxide and basic zinc carbonate.

From a quantity of gas standpoint, the theory becomes almost untenable when the practical and effective additions of retardants are compared with the amounts of non-flammable gases produced by the decomposition of cellulose itself. Experimentation¹⁴ shows that none of the well-known retardants produce inert gases in quantities of magnitude much greater than the fabric alone. Despite this, however, the theory has been widely accepted. The results given in Chapter II certainly do not substantiate this mechanism as of prime importance in the flameproofing of fabrics, although it may contribute somewhat to the over-all retardation.

4. THERMAL THEORIES

It has been proposed that flameproofing may be explained on a thermal basis whereby fabric temperatures "in situ" are retained below the dissociation point. Two major concepts are prevalent, the first of which presumes that the calorific input of an incident heat source may be dissipated by an endothermic change in the retardant itself. Thus the fusion, sublimation or decomposition of the retardant as well as any further phase transitions of retardant mixtures might absorb considerable energy which otherwise would contribute to the amount required for activation of the

¹³ Leatherman, M., Maj., C.W.S., "Flameproofing of Permeable Military Clothing," Memorandum Report, T.D.M.R. No. 936, Project No. D31-1, Edgewood Arsenal, Md. (Nov 25, 1944).

¹⁴ Tyner, H. D., "Fire Extinguishing Effectiveness of Chemicals in Water Solution," *Ind. Eng. Chem.*, 33, 60-5 (1941).

fabric. The second hypothesis supposes that the incident heat may be conducted away from the fibers at a rate comparable to that at which the source supplies it, and thus by effects similar to those encountered in the Davy Safety Lamp the fabric in the vicinity of the edge of the flame never reaches its combustion temperature. However, although little or no experimental evidence has been forwarded for this hypothesis, it would appear that since only small amounts of certain materials are required to be effective as retardants they would have to be extremely efficient in their heat-dissipating capacity in order to substantiate the theory. Moreover, there exist a number of salts which are ineffective as retardants although their energy changes are similar to those of the efficient salts. These non-retardants have little or no practical flameproofing value when added in moderate amounts to a fabric and even upon the addition of excessive quantities they will not prevent flame propagation and at most only reduce the rate at which the fabric is consumed. Furthermore, the known heat conduction constants for materials of widely divergent retarding power are either quite similar or are not sufficiently different to account for their dissimilar flameproofing qualities.

Further verification of the inadequacy of this theory to explain the facts is found by a detailed study of the phase transitions involved in the thermal behavior of a large number of retardants when heated to temperatures in the vicinity of that attained by burning fabric. When these salts are heated at a constant rate and the differential heating curve determined for equal quantities of retardant components and mixtures, the number of inflections and their magnitude may be taken as being directly proportional to the heat-absorbing capacity of the system. Phase data, similar to that depicted in Figure 3, for a large number of materials show that no correlation exists between the number, position and magnitude of the energy changes and the relative ability of the materials to prevent flame propagation. In fact, some of the better retardants undergo only minor transitions and in the case of the fairly efficient ammonium sulfamate-phosphate mixture even an exothermic change is observed.

A study of the thermal behavior of fabrics when decomposed via the experimental method previously described in Figure 24 of Chapter II shows that the phase and energy changes take place in several distinct steps. When conducted in either nitrogen or CO_2 atmosphere, an initial heating period is observed accompanied by evolution of some water and gas during which the fabric is raised to about 300°C . Following this, a rapid reaction proceeds with the usual tar and gas elimination which takes place isothermally. However, in the presence of air, the initial induction period is succeeded by a rapid exothermic reaction, coincident with tar evolution, wherein the fabric temperature rises to from 500 to 700°C . depending upon the velocity of the air supply. The intensity of this spontaneous reaction appears to be independent of variance of the initiating

temperature in the range of 300 to 500° C. Hence, any retardant functioning as an energy absorber or diffuser would be required to maintain fabric temperatures below 300° C. to prevent continued burning. Following the tar evolution, the temperature falls for a short time until the residual char begins to undergo the secondary exothermic oxidation which coincides with the afterglowing properties of the material. The latter re-

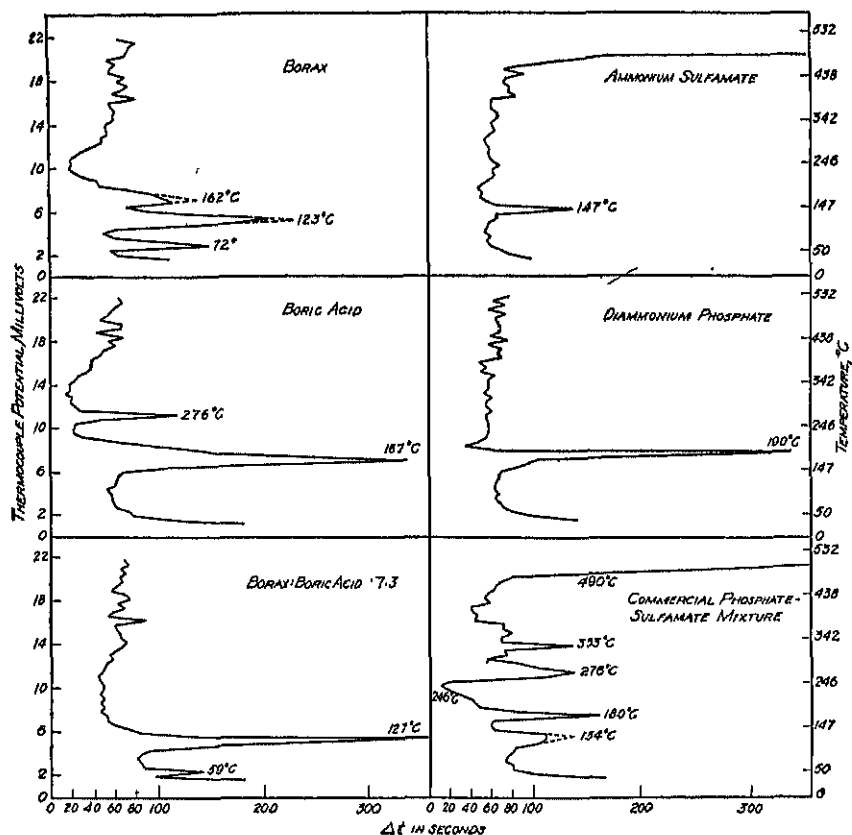


Figure 3. Phase transitions occurring during the heating of various retardants and the energy changes involved in these transitions.

action, however, is a separate phenomenon and is not pertinent here, but is discussed fully in a later chapter. It is the primary dissociation and oxidation that is directly responsible for the flaming characteristics of the fabric, and as shown in Figure 4, the intensity and duration of this initial reaction appear to be unrelated to the good flame-retarding characteristics of small amounts of the borate mixture. In all cases the initial reaction proceeds with maximum intensity in the neighborhood of 500° C., and it is only with excessive amounts that slight physical effects are observed.

Similar behavior is exhibited by fabrics treated with other retardants, and no conclusive evidence appears in support of the thermal theories.

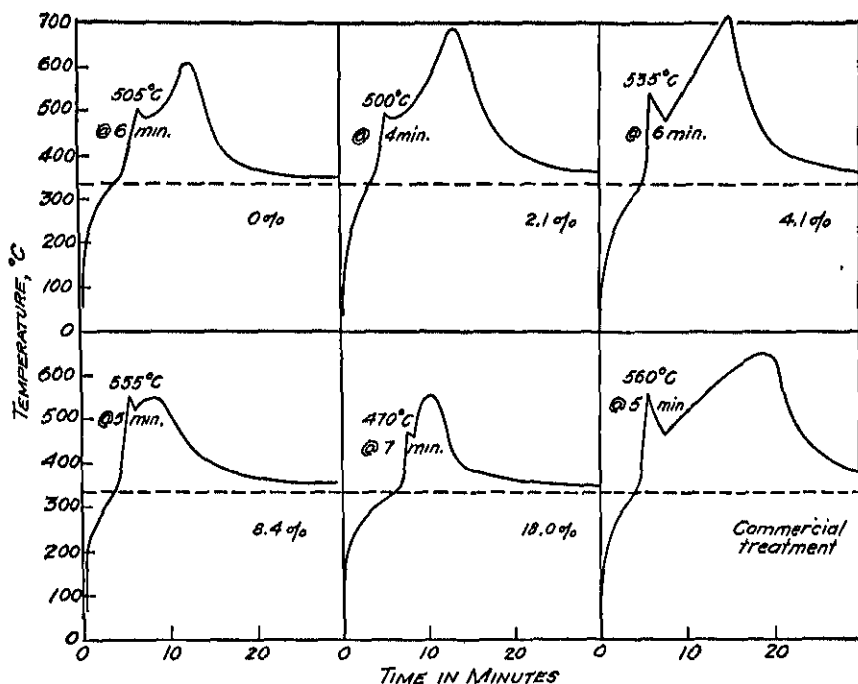


Figure 4 The thermal behavior of fabrics treated with borax-boric acid 1:1 when heated at 330° C. in the presence of air. The per cent values are those added to de-sized twill and the temperatures are those maxima attained in the primary dissociation reaction.

B. PREVENTION OF AFTERGLOW

1. CHEMICAL THEORIES

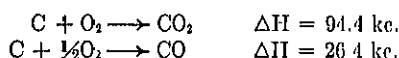
It is apparent that the glowproofing of fabrics is directly concerned with the oxidation of carbon which is the main constituent of the charred residues which undergo this reaction. Studies attempting to elucidate the prime cause for the phenomenon have discouraged investigation due to the limited number of compounds which exhibit good retarding effects. However, some light is cast on the problem by considering those materials which actually enhance the glowing characteristics of cellulose. Here it should be remembered that although such materials as stannic oxide inhibit flaming combustion they render fabric particularly sensitive to consumption by flameless combustion. Similarly, Kramer¹⁵ has found that many metallic oxides have a catalytic action on the oxidation of carbon

¹⁵ Kramer, W. A., "The Catalytic Oxidation of Carbon," Thesis, Ph.D., Ohio State University (1927).

such that the ignition temperature is much lower in their presence, burning proceeds much more rapidly. Furthermore, Whitesell and Fraser have shown that although manganese dioxide catalyzes the oxidation of carbon monoxide, its influence is dependent upon traces of alkali, when the oxide is prepared free from absorbed alkali the catalytic action on the oxidation is greatly increased. It would appear then that at least enhancement of the glowing characteristics imparted to fabrics by metallic oxide type of flameproofing may be attributed to catalytic candescent oxidation of carbon following its formation as a char on flame-inhibited cellulose, and that this catalytic activity is extremely sensitive to poisoning by alkali.⁹

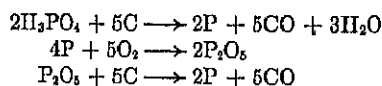
The above phenomena have direct analogies in the field of glow retardation. Here, as has been shown in Chapter II, although boric acid and ammonium phosphate in very small amounts prevent glow, their mixtures with sodium tetraborate are not effective unless the boric acid or phosphate is in excess. The retardation process is hence likewise susceptible to poisoning by alkaline salts. The evidence is therefore in favor of a single catalytic influence on the course of the oxidation of carbon to count for both the enhancement and retardation processes.

One of the simplest mechanisms whereby such activity would function appears to be a change in the course of the oxidation favoring a path of lesser exothermicity than normal.¹⁷ For instance, if the oxidation is promoted in the direction of CO formation rather than of CO₂ formation, the heat of the reaction is reduced from 94.4 to 26.4 kilocalories per mole,



The inference is then that the first reaction is the self-sustaining glow reaction, while the second, in which the energy change is considerably lower, is the course taken by glow-retarded fabrics, where the heat liberated is insufficient to propagate the oxidation after the instigating source is removed. This theory presumes that the retardants accelerate the formation of carbon monoxide and decelerate that of carbon dioxide when char residues are subjected to heat, and is in complete accord with the experimentally observed effects given in the previous chapter.

The catalytic mechanism favoring the preferred reaction may involve changes in energy barriers (heats of activation) for the two reactions and may proceed by the following set of reactions:¹⁷

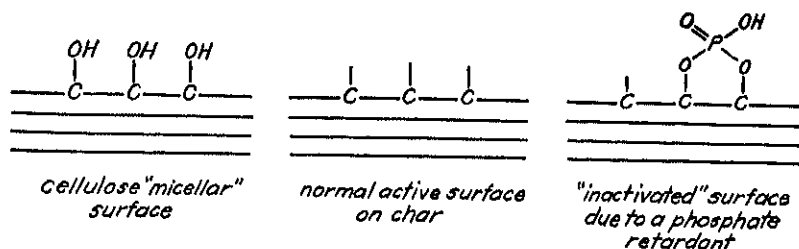


¹⁶ Whitesell, W. A., and Fraser, J. C. W., "Manganese Dioxide in the Catalytic Oxidation of Carbon Monoxide," *J. Am. Chem. Soc.*, 45, 2841-51 (1923).

¹⁷ Sisson, W. A., Paper presented at Office of Quartermaster General, Conference on N.R.C. Project Q.M.C. # 27, Washington, D. C. (Dec. 15, 1944).

Here the phosphate directs the carbon to the monoxide form and is regenerated, the net heat liberated in the series of reactions being considerably less than the direct oxidation to the dioxide.

Another possibility is that the active centers on the carbon char may be taken up by the retardant, thus lessening its activity. The surface sorption may be similar chemically to the well-known graphitic acid type such as graphitic bisulfate or fluoride, and the following illustrates a possibility:



Sketch of fixation of phosphate to cellulose micelle.

The tenacity with which the glow retardants are held on the char further indicates that the mechanism is associated with a surface catalytic phenomenon, but the data are insufficient to determine the type of sorption involved.

2. PHYSICAL THEORIES

The anti-glow properties imparted to carbonaceous residues resulting from the flaming combustion of fabrics have been attributed to a fluid incombustible layer which coats the carbon surface to protect it from direct contact with the oxygen of the air. The mechanism is assumed to be identical with a similar theory advanced to account for the inhibition of afterflaming, but suffers in the light of the well-known fact that some retardants have excellent flame- but no glow-retarding influences and vice versa. A typical example is the borax-boric acid system, where the acid protects cotton from afterglow but has little or no effect on the flaming characteristics. On the other hand, borax has a fairly efficient flame-retarding action but shows no flameless combustion inhibiting effects. Mixture of the two materials provides protection from flame but not from glow, despite the fact shown by Ramsbottom and Snoad¹ that the mixtures produce a much better covering and uniformity of coating than the components alone. Similar anomalous behavior is exhibited by the borax-diammonium phosphate system, and it is apparent that the hypothesis falls down upon critical analysis.

In the case of the metallic oxide-chlorinated body system of flameproofing, the latter component is advocated⁶ as serving the function of not

only binding the oxide to the fabric but also of inhibiting the glowing tendencies. The coating property of the chlorinated paraffin or resin is assumed either to prevent oxygen infiltration or on decomposition to disperse the ambient oxidizing atmosphere with HCl. Again, these theories are untenable in the light of the facts, since experimentation has shown that even with exceedingly high additions of a wide variety of these chlorinated compounds, with or without metallic oxides, they exhibit no true glowproofing effect. It appears, however, that large amounts of these compounds serve in some measure to reduce slightly the rate at which flameless combustion is propagated in the char and they do actually reduce the tendency for advance of glow into uncharred areas of the fabric. However, they cannot be considered anti-glow reagents in the same sense as the efficient boric and phosphoric acids or substances which produce the same effect as the two latter materials during contact with the flame.

The further purpose attributed to anti-glow reagents, in that they are assumed to utilize a thermal conduction or insulation function, is likewise not supported by the evidence. When charred fabrics are prepared by pyrolysis in a carbon dioxide atmosphere in the equipment of Figure 2, Chapter II, and then heated in a stream of air, their thermal behavior may be observed. The rate at which a thermocouple embedded in the char attains a temperature maximum characterizes conductance and oxidizing tendencies, and it is found that although all salts retard the rate and extent of temperature elevation, there is little if any correlation between these thermal effects and the glow-retarding properties of the salts, except when these materials are added in large amounts. An example of this type of behavior is illustrated in Figure 5, where effects shown by the excellent glow retardant $\text{NH}_4\text{H}_2\text{PO}_4$ are similar to those exhibited by the good flame- but poor glow-retardant mixture of borax and boric acid in a ratio of 1 : 1. This contrary behavior is further accentuated by the fact that less than 1% of ammonium phosphate will prevent glow in a charred fabric, and that additional amounts are unnecessary provided other organic substances are absent.

At high temperatures the thermal properties of charred residues from previously treated fabrics are however quite different, and the insulation value of these chars is directly attributable to their glow-resistant quality. This property is not directly dependent upon the added retardant but upon the function of the carbon itself. This is shown by the behavior of fabrics when subjected to various conditions in the equipment in Figure 6, p. 10. Here either flames of a reducing or oxidizing nature or air blasts at various temperatures may be allowed to impinge on fabrics and the resultant temperature at various distances from the opposite face determined. Experimentation shows that flameproofed fabrics, subjected to heat sources of intensity greater than 1000°C . offer resistance to heat transfer so that the ambient temperatures below the fabric are reduced.

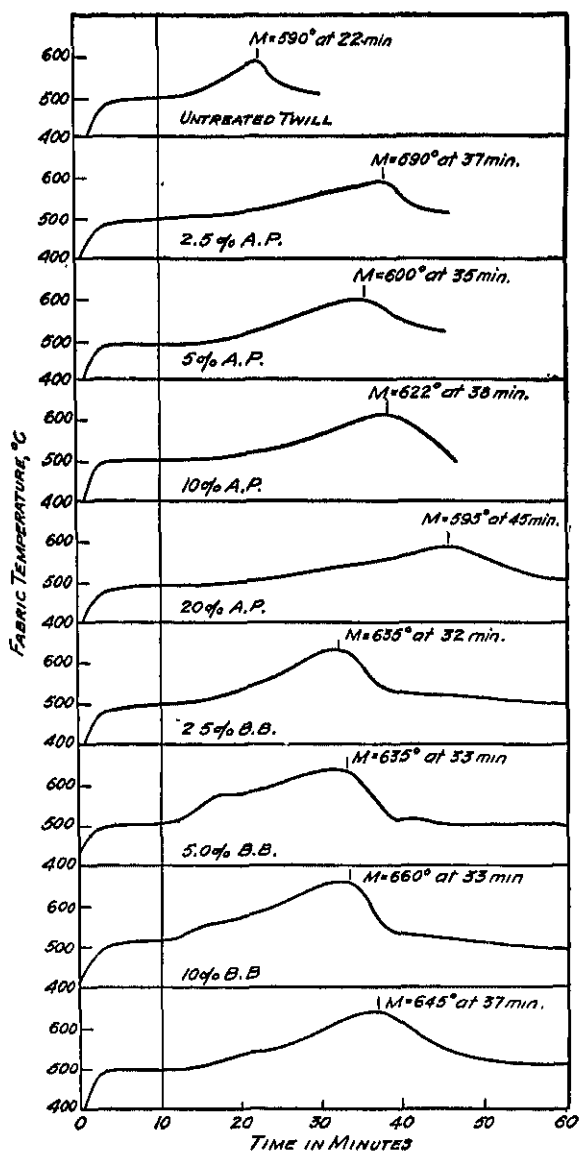


Figure 5. The thermal effects in the oxidation of charred fabrics (Fabrics heated in CO_2 atmosphere for 10 minutes, thence in air) The per cent values are the additions of A.P. ammonium phosphate, and B.B. borax-boric acid 1.1. *M* denotes the maximum temperature attained.

considerably, and that glowproofing increases the period over which this protection is effective. This effect is observed irrespective of the nature and intensity of the heat source, since reducing and oxidizing flames as well as air blasts from 600 to 1000° C. give similar results. The rate of temperatures attained under the glowproofed fabrics compares favorably to that attained with asbestos paper of similar thickness. Similarly, with air blasts at 800° C., the time required to reach 200° C. at $\frac{1}{4}$ inch below

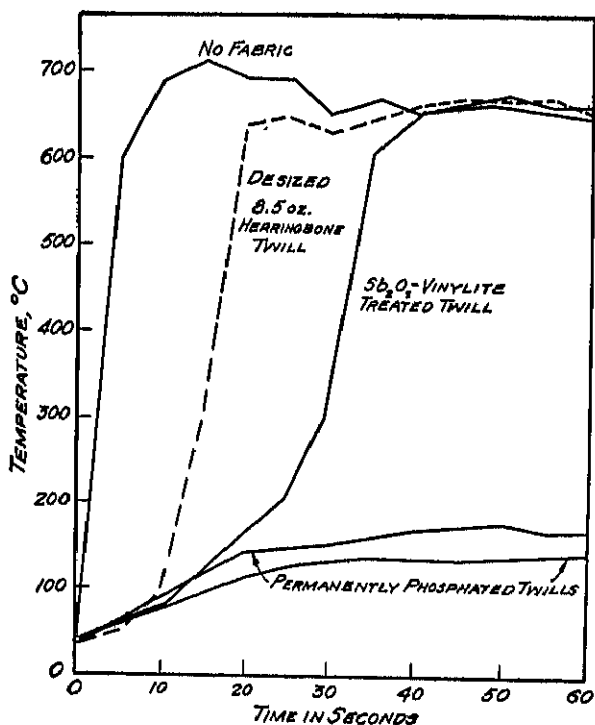
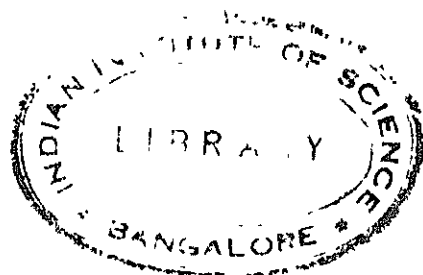


Figure 7. The effect of glow retardation on the insulation afforded by fabrics. The temperatures are those attained in "dead air" $\frac{1}{4}$ inch behind the fabric, with an ambient external temperature of 600–700° C.

these non-glowing fabrics is equal to or greater than that for glass-asbestos or glass-neoprene fabrics either alone or when plied, indicating a higher insulating value for the flameproofed cotton fabrics. An example of the behavior of various fabrics is shown in Figure 7. These differences result from the variance of the type of oxidation pursued by the charred residue. With the glowproofed type, the char, retaining all of the fabric-character of the original material is oxidized slowly and uniformly by the source and at no point does it even attain incandescence. The non-glowproofed type, however, attains a white heat and decomposes with rapidity in

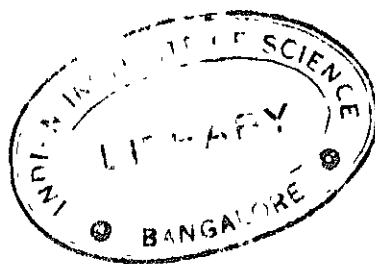
various locations allowing for intense radiation, and very soon the char crumbles allowing the full blast of the incident source to penetrate the material. The insulation is directly dependent upon the retention of a non-penetrable fabric-like structure where the "dead-air" space and the normal low thermal conductivity of carbon function to retard calorific transfer. It is only in an indirect manner that the retardant itself acts in the conductivity barrier via its effect on the type of oxidation pursued by the carbon. In the case of the metallic oxide coatings, however, it appears that the incandescent particles of the flame retardant may contribute to their especially poor insulation effects by enhancing radiation.

The actual physical nature of the carbonaceous residues are not governing factors in their glowing characteristics as shown in the previous chapter, and from the above it would appear unlikely that the glow-retarding phenomena could be induced by the retardant via purely physical means.



Section Two

METHODS



Chapter IV

Test Methods for Evaluation

An ideal flameproofing agent might be defined as that material which when present in very low add-ons is capable of rendering a fabric completely and permanently resistant to both afterflaming and afterglow without adversely affecting any of the other desirable fabric characteristics. The merit of a flameproofing agent, then, may be considered as being primarily dependent upon its ability to effectively prevent afterflaming and afterglow. Its practical value, however, is also governed by the extent to which it may impair other desirable fabric properties such as hand, strength and the permeability of the cloth to air and moisture vapor. In addition, its practical significance is further dependent upon the permanence of the flameproofness attained as indicated by the resistance of the treated fabric to leaching and laundering and the ionic exchange reactions produced by exposure to excessive perspiration or immersion in sea water. Finally, considering the application to clothing fabrics it is important that the added flameproofing treatment does not increase the heat load imposed by a garment upon the wearer nor produce any other undesirable physiological effects.

In the light of these functional requirements, it is evident that in initiating any experimental program for the investigation of flameproofing agents it is essential that suitable laboratory test methods be available for proper evaluation of the retardants developed and classification as to comparative efficiencies. Any amount of research on new or improved methods of flameproofing will be of little value if the products developed cannot be quantitatively compared with contemporary treatments both with respect to the initial flameproofness achieved and the influences exerted upon other desirable fabric properties. An attempt has been made in this chapter to assemble representative laboratory test procedures as would be required in order to properly evaluate flameproofing agents or treated fabrics. In order to illustrate the significance of the tests described and at the same time outline a suggested program for the comparative evaluation of flameproofing materials, the test procedures are preceded by a description of the performance requirements established for the laboratory investigation of flameproofing agents or flameproofed fabrics.

A. EVALUATION REQUIREMENTS

Robert W. Little

A comprehensive study of the performance characteristics of a flameproofing agent is generally a detailed and time-consuming process. Since, in the course of developing new retardants or evaluating the materials proposed by other investigators, it is often desirable to obtain a rapid initial estimate of the effectiveness of a treatment, the evaluation program employed in the experimental work of N.R.C. Project Q.M.C. #27 included a shorter, less extensive study intended to give a preliminary appraisal of the effectiveness of a retardant. In the event that the material tested demonstrated superior performance in these preliminary experiments, it was then committed to the extensive complete evaluation. The specific tests included in any particular instance are dependent upon whether the material being evaluated is available in the form of the flameproofing agent itself or only as a processed fabric and also upon the expected durability of the retardancy obtained.

Since the flameproofing agents which may be encountered fall rather naturally into the categories of temporary and durable treatments, it is well to consider the evaluation procedure for each of these two cases separately.

I. PRELIMINARY EVALUATION

a. Temporary Treatment

In the event that the flameproofing agent itself is available for evaluation it is desirable to obtain a rough approximation of the minimum add-on requirements for effective flameproofing. To achieve this, two 12 by 20 inch samples are impregnated with add-ons of 10 and 20% by immersion in solutions of these same percentage concentrations followed by squeezing to a 100% wet pickup.

Flame Tests. The two samples, treated as described above, are conditioned for at least 24 hours at 70° F. and 65% R.H. and subjected to the 45°-Microburner and Vertical-Bunsen burner flame tests, using duplicate specimens in each case. The flame test data is recorded in terms of after-flame time in seconds, time of afterglow in seconds, and char area or char length in square inches or inches respectively. On the basis of these initial flame tests, the lower effective add-on is selected and employed in the preparation of treated fabric for use in the remainder of the preliminary evaluation tests.

When the material being evaluated is in the form of previously processed fabric, one 12 by 20 inch sample is taken and specimens cut for

duplicate measurements in the 45°-Microburner and Vertical-Bunsen flame tests. In this case the same treated fabric is employed in subsequent evaluation tests.

In order to avoid repetition, references to the "flameproofed fabric" or "treated fabric" in the following discussions will be construed as meaning the treated fabric either as received or as impregnated with the approximate minimum effective add-on previously determined.

Tendering Tests. In order to determine the extent of any loss of fabric strength caused by the impregnation process, standard tensile test measurements are carried out on both the untreated and treated fabric. This requires a fabric sample 6 by 12 inches in each case in order to provide triplicate measurements by either the grab or raveled strip tensile tests. Measurements are made in the direction of the warp threads only.

These preliminary tests of a temporary flameproofing treatment afford a rough estimate of its flameproofing efficiency and the effect of the process upon the fabric strength.

b. Durable Treatments

Leaching Tests. In the case of flameproofing treatments of a more or less durable nature, the above evaluation procedure is supplemented by a few simple leaching experiments. The additional specimens required increase the size of the original sample to be impregnated or cut from the treated fabric, whichever the case may be, from 12 by 20 inches to approximately 21 by 23 inches. The initial flame tests are performed as described above for the water-soluble type, employing higher add-ons of 20 and 40% respectively. Again, the lower effective add-on is selected and that fabric employed in subsequent evaluation tests. In addition to triplicate tensile strength measurements as performed with the temporary treatments, single 7 by 7 inch specimens of the treated fabric are also subjected to each of the following leaching experiments:

1. 30-minute immersion in distilled water with constant stirring.
2. 5-minute immersion in 5% sodium chloride solution, followed by wringing out excess solution, conditioning 24 hours at 70° F. and 65% R.H. and leaching for 30 minutes in running tap water.
3. 1, 3 and 6 launderings in 0.5% G.I. soap.¹

Following the leaching and laundering treatments, the specimens are air-dried, conditioned and subjected to the 45°-Microburner flame test, noting the times of afterflame and afterglow and measuring the char area.

These few simple tests provide for a preliminary estimate of the efficiency of a durable-type treatment in terms of its initial flameproofing

¹ The soap listed here and elsewhere in this volume as "G.I. Soap" is that supplied by the Quartermaster Corps as Soap, ordinary issue; Specification JCQD No. 1008A, Sept. 17, 1945 (Stock No. 51-S-1644).

characteristics, the effect of the impregnation process upon fabric strength and the resistance of the flameproofness to leaching, ion-exchange and laundering.

2. COMPLETE EVALUATION

Once a flameproofing treatment has been studied by means of the experiments just described and shown to be fairly effective, it may be considered worthy of more extensive investigation. In this case, the complete evaluation procedure includes a much more detailed survey of the initial flameproof characteristics of the fabric, the variation in fabric strength which may occur and the resistance of the treatment to leaching, laundering and sea water immersion. Furthermore, a study is made of the relative resistances of the treated and untreated fabrics to the passage of moisture vapor and the effects of high temperatures and humidities upon the strength and flameproofness of the treated fabric.

a. Temporary Treatments

Flame Tests. When the flameproofing agent itself is available for study, five 16 by 26 inch samples are treated with add-ons of 5, 10, 15, 20 and 30% respectively by immersion for a 100% wet pickup in solutions of these percentage concentrations. After air-drying and conditioning, the samples are cut into test specimens and tested in quintuplicate using both the 45°-Microburner and Vertical-Bunsen flame tests. On the basis of the flame test performance, a minimum effective add-on is selected and sufficient fabric impregnated with this amount of retardant to serve for the remaining evaluation tests.

Where the flameproofing treatment is available only in the form of treated fabric, one 16 by 26 inch sample is taken and used for quintuplicate measurements in the 45° and vertical flame tests. It is assumed in these cases that the add-on applied to the fabric was close to optimum for the particular process. A sample of treated fabric approximately 30 by 190 inches is required for the remaining tests of a complete evaluation.

Tendering Tests. Sextuplicate tensile strength measurements are carried out by means of either the grab or strip test on the treated and untreated fabric and also on the treated fabric after it has been exposed to the following conditions:

1. 2 weeks' storage at 120° F., 85% R.H.
2. 2, 3 and 4 weeks' storage at 150° F., dry.

These accelerated conditions are intended to simulate the extremes which might be encountered in the course of normal use and storage. They were designed primarily for the testing of flameproofed fabrics intended for use in articles of Army clothing.

In addition to these tensile strength measurements, the effect of the tendering conditions upon the flameproof characteristics of the treated fabric is also determined by running triplicate 45°-Microburner flame tests on specimens which have been exposed to 1. and 2. above.

Moisture Vapor Permeability. The resistances of both the untreated and treated fabrics to the passage of moisture vapor are determined. This requires nine 4 by 4 inch specimens in order to determine the specific resistances of 1-, 3- and 5-layer assemblies. The intrinsic resistance is calculated in each case and the relative permeability of the treated fabric expressed in terms of the percentage deviation of its intrinsic resistance from that of the untreated material.

b. Durable Treatments

Leaching Tests. With flameproofing treatments which are intended to be of a more or less permanent nature, the above tests are supplemented by rather extensive leaching and laundering experiments. Triplicate 7 by 7 inch specimens of the treated fabric are subjected to each of the following conditions:

1. 30-minute immersion in distilled water with continuous stirring.
2. 24 hours' immersion in running tap water.
3. 2 hours' rotation in synthetic sea water.
4. 1, 3 and 6 launderings in 0.5% Igepon-T.
5. 1, 3 and 6 launderings in 0.5% G I soap.
6. 1, 3 and 6 launderings in 0.5% G I. soap + 0.2% Na_2CO_3 .

The leached or laundered specimens in each case are air-dried, conditioned for a minimum of 24 hours in the standard atmosphere and tested by means of the 45°-Microburner flame test, notation being made of the usual characteristics of afterflame time, afterglow time and char area.

The complete evaluation procedure outlined in the preceding pages provides a fairly thorough appraisal of the performance of a flameproofing agent as applied to textile fabrics. The retardant is classified as to the initial flameproofness produced, the minimum effective add-on required and the effect on permeability characteristics of the fabric. Furthermore, an insight is gained into the losses of fabric strength or flameproofness which may result upon exposure of the treated fabric to extremes of temperature or humidity such as might be encountered in the course of use or storage. Finally, when the treatment under consideration is of the durable type, the extensive leaching tests indicate the relative resistance of the treatment to solubility and ion-exchange reactions and the degree of alkalinity which the fabric will withstand in laundering solutions.

If a retardant treatment is intended primarily for use in clothing fabrics and, on the basis of the above evaluations appears to very nearly satisfy the requirements for an ideal treatment, additional, more specific

tests may be employed. Included in this group would be the laboratory test for determining the resistance of flameproofed fabrics to excessive perspiration. The final decision as to the suitability of a treatment for use in articles of Army clothing would rest upon the outcome of a series of practical field tests. In these performance experiments, the treated cloth is actually fabricated into garments and worn by men under normal and accelerated conditions simulating those which might be experienced in the course of actual military operations. Wear tests of this type are intended to determine the length of service which a garment may be expected to give, the increase which the added treatment may produce in the heat load imposed by the garment upon the wearer or the nature and extent of any toxic effects which the flameproofing agent may exhibit.

In the following section on test procedures, the tests employed in the laboratory evaluations of flameproofing materials, as well as the supplementary tests suggested, are described in order to define the conditions under which the experimental data presented in later chapters was actually collected. In addition, it is hoped that the presentation of these testing procedures will aid in the standardization of selected methods for use in future investigations of flameproofing materials.

B. TEST PROCEDURES

1. LABORATORY IMPREGNATIONS

Robert W. Little

The efficiency of any compound or mixture as a flameproofing agent may be predicted on the basis of its chemical and physical properties and its performance in a number of more or less fundamental laboratory tests. The final decision as to its effectiveness in comparison with known and tested retardants, however, must be based upon practical flame test evaluations of a fabric to which the agent has been applied. It is apparent, therefore, that the method of applying the flameproofing agent to the fabric is of nearly as great importance as the flame test employed in evaluating the treated cloth. The uniformity with which a retardant is applied and the degree of penetration achieved will greatly influence the performance in subsequent tests and hence prejudice the rating which the agent may be assigned in comparison with other flameproofing materials. To obtain a true picture of the relative efficiencies of a group of flameproofing agents, it is imperative that all the members of the group be given an equal chance through a consistent and effective impregnation technique. In the following sections are presented the recommended procedures for the application of flameproofing agents to test fabrics on a laboratory scale. The apparatus is limited to the simplest types of labora-

tory equipment in order to be of help to the greatest number of investigators. Obviously, more uniform and effective applications can be attained through the use of small-scale commercial equipment such as a Butterworth padder. However, the exact nature of the treating apparatus is secondary in importance. The primary requirement is that the same equipment and technique be employed in all cases where comparisons of test data and relative efficiencies are to be made.

a. Single-Bath Applications

This method of applying flameproofing materials to woven fabrics from a clear solution of the retardant is applicable to those agents which are soluble in organic solvents as well as to the aqueous solutions of the more common water-soluble retardants.

To aid in attaining uniformity of treatment among specimens which are to serve as multiplicates in one of the evaluation tests, a strip of fabric is cut which can be processed as a unit rather than treating each specimen individually and introducing additional variables into the comparisons. Prior to impregnation, the fabric strips are conditioned for at least 24 hours at 70° F. and 65% R.H. and weighed, in order to obtain a control weight of the fabric for accurately determining the add-on obtained. The conditioned strips are then soaked for a total period of approximately 5 minutes in an appropriate volume of the retardant solution of the desired concentration. During the soaking period, the strips are passed twice through a simple hand wringer returning the fabric to the bath each time. The wringer should be set so that the weight of the wet treated fabric is just double that of the untreated strip. This constitutes a 100% pickup and indicates that the treated cloth then contains an amount of retardant expressed in per cent approximately equal to the percentage concentration of the treating bath. The strip of fabric is passed through the wringer a third time and weighed approximately to check on the wet pickup obtained. If the fabric contains too little or too great an amount of retardant, the wringer should be adjusted correspondingly and the reimmersed strip passed again through the rolls. With a little experience, the wringer can be calibrated and accurately set for a 100% wet pickup. The treated strips are finally air-dried and again conditioned for at least 24 hours at the standard atmosphere. A final weighing is made to obtain the apparent dry add-on of the flameproofing agent.

In the case of the temporary type of water-soluble retardants, the treated fabric is now ready to be tested. With some of the more durable treatments, such as the urea-phosphate type, the flameproofing agent is applied from aqueous solution as described above but requires subsequent curing and washing before the fabric is conditioned and weighed to determine the add-on.

b. Double-Bath Applications

As described above, strips of the fabric to be treated are cut, conditioned for 24 hours in the standard atmosphere and weighed. The sample strips are then soaked for a period of 5 minutes in an appropriate volume of a solution of the first reactant in the double-bath process, being passed through a hand wringer twice during the soaking period. The samples are then passed between the rolls a third time and weighed to insure a wet pickup of approximately 100%. After air-drying, this procedure is repeated using a solution of the second reactant. When several strips of fabric are treated simultaneously, a fresh portion of the second solution should be used for each sample strip. The treated samples are then subjected to a 15-minute leach in running water to remove the unreacted water-soluble salts. After conditioning for a period of not less than 24 hours the strips are again weighed to determine the dry add-on obtained and are ready to be tested.

c. Suspensions or Emulsions

The prepared impregnating mixture is placed in a V-shaped trough which is held adjacent to a hand wringer and is constructed in such a manner that the drippings from the rolls run back into the treating bath. A bar or roller at the bottom of the trough serves to hold the fabric immersed while passing through the bath. Strips of fabric, which have been conditioned and weighed, are drawn slowly through the retardant mixture by means of the hand wringer, the rolls of which have been set according to the add-on desired. With emulsion and suspension applications it is often more desirable to adjust the final add-on by varying the pressure of the wringer rolls rather than changing the concentration of the bath. For this reason the desired wet pickup may be other than 100%. In any case, the pressure to be applied in wringing must be determined by experimentation and it is well to determine the correctness of the pressure used by weighing the wet strips as they leave the wringer. The strips of fabric are passed through the bath and wringer three consecutive times, air-dried to remove the bulk of the volatile organic materials, and finally dried in an oven at 100° C. for 10 minutes to remove the last traces of solvents. After conditioning for a 24-hour period in the standard atmosphere and weighing to determine the dry add-on obtained, the treated fabric is ready to be cut into specimens and tested. The same trough and general method of treatment can be used in the application of resin coatings to flameproofed fabrics. In this case, however, a single pass through a dilute resin solution is sufficient.

There are many types of flameproofing agents which require special

application techniques and cannot be applied by the methods outlined in the preceding sections. In general, however, the majority of the better flame- and glow-retardant treatments may be applied to fabric by one of the techniques described. The fundamentals of these laboratory methods of impregnation closely resemble the type of processes which can be handled on commercial apparatus currently existent in the textile industry. Flameproofing treatments which require very special equipment and techniques for application to the fabric may not be exploited because of the scarcity of special large-scale equipment of a similar nature in the finishing plant.

2. FLAME TESTS

Robert W. Little

In any study of the characteristics of flameproofed textiles the flame test employed in evaluating the flame- and glow-resistant characteristics of the fabric is of the utmost importance. The selection of a proper test procedure must be based upon a careful consideration of the type of fabric being used, the nature of the flame exposure to which it may be subjected in the course of service, and the requirements as to flameproofness which the treated fabric is expected to meet.

It is essential that the investigator be aware of just what property of the treated fabric he is desirous of evaluating. In the case of treated fabrics which are flame resistant, but might not be classified as truly flameproofed, the characteristic to be measured may be the inflammability or ease of ignition. It may be, on the other hand, that the most interesting property is not the ease of ignition, but rather the rate at which the fabric burns once ignition has been accomplished. This might be termed combustibility. With efficiently treated materials the property to be tested would be the general flameproofness of the fabric. The requirements of a test for quantitatively determining relative flameproofness, inflammability or combustibility would be very different in each case.

Considering the flame tests commonly employed in the testing of flameproofed fabrics, the observations recorded serve to estimate the degradation suffered by the specimen through three different mechanisms. The char area or char length measurement serves as an index of the total damage suffered by the fabric, while in contact with the igniting flame and also resulting from extended afterflaming or afterglow. The time of afterflaming in seconds is a measure of the extent of decomposition caused by autocombustion after the igniting flame has been extinguished. Finally, the duration of afterglow serves as an estimate of the damage suffered through oxidation of the charred residue and adjacent fabric once all flaming has ceased. Which of these flameproof characteristics is considered to be the most important will largely govern the selection of a proper

flame test and will be dependent upon the end use and performance requirements of the fabric being considered. It cannot be emphasized too strongly that the selection of the proper test apparatus and procedure is dependent upon the anticipated use of the fabric and the requirements to be satisfied. A flame test which is too severe or too mild may give an entirely erroneous picture of the relative efficiencies of flameproofing agents for a specific application.

A great number of laboratory burning tests have been developed for estimating the relative flame and glow resistance of flameproofed fabrics. For a complete picture of the tests developed and the details of their manipulation the reader is referred to the technical, trade, and patent literature on the subject.^{2, 3} An attempt will be made in the following pages to present a brief outline of the best of the available tests, emphasizing those which show special merit and appear to be most widely applicable.

a. Tests for Relative Inflammability

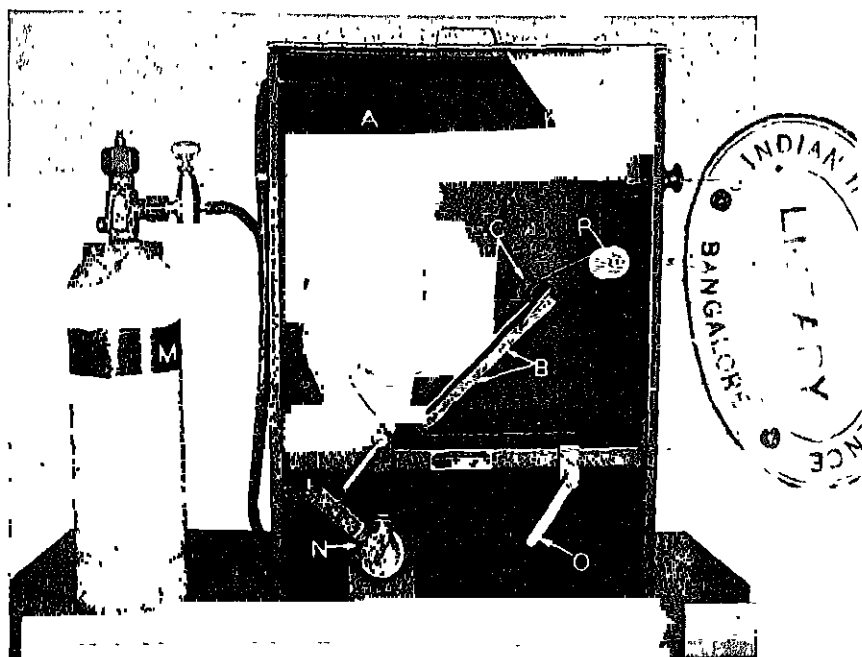
Under the pressure of current legislation in the state of California and impending federal legislation, this test has recently been developed by a special subcommittee of the American Association of Textile Chemists and Colorists. This committee on Flammability of Consumer Textiles was charged with the responsibility of developing a test method and apparatus which would serve to measure the relative inflammabilities of consumer fabrics and hence afford a means of differentiation between hazardous and non-hazardous fabrics. The definition of a given flaming time in seconds as signifying a dangerously inflammable fabric is obviously a difficult and responsible task and one which would require the careful comparison of test data obtained cooperatively by many different operators. This correlation work is still in progress and hence the final details of the test method and performance requirements have not yet been stated. The test is unique at the present time, however, and warrants presentation as far as the details have been established. It is readily apparent that a test of this type would not be applicable to the testing of truly flameproofed fabrics. It is primarily intended as a means of differentiating between various untreated fabrics, classifying them as somewhat hazardous or highly hazardous based upon their burning characteristics.

A.A.T.C.C. Flammability Test. The apparatus as it now stands is shown in Figure 1. It has been developed to be completely automatic, eliminating nearly all the personal error attributable to the operator. The specimen rack is adjustable in order to compensate for the differences in

² "The Fireproofing of Textiles." Research Rept. of Textile Research Institute, Inc. (July, 1943).

³ "Recommended Requirements for Flameproofing of Textiles." National Fire Protection Assoc., Boston, Mass. (1941).

fabric thickness. A specimen shield is provided to hold the test specimen flat on the rack and prevent curling once flaming begins. The shield at the same time eliminates any possible edge effects by covering the cut edges of the specimen.



Courtesy of American Association of Textile Chemists and Colorists.

Figure 1 A.A.T.C.C. Flammability Tester

- | | |
|---|---|
| <p>A. Draft-proof chamber with adjustable top.</p> <p>B. Specimen rack, fixed at an angle of 45°, consisting of a 4 by 7 inch framework laced horizontally with heat-transmitting wire.</p> <p>C. Specimen shield which covers all but a 1.5 by 6 inch strip of the test specimen</p> <p>D. Indicating finger, by means of which the thickness of the sample is compensated for in the throw of the gas nozzle.</p> <p>P. Gas nozzle.</p> | <p>G. Stop cord which determines vertical flame height.</p> <p>H. Guide for stop cord.</p> <p>I. Stop weight, clipped to cord.</p> <p>J. Control for holding sliding door open</p> <p>K. Slide door (shown in end view) normally slides in the grooves at the front of the cabinet</p> <p>L. Fuel control valve (used in conjunction with a flowmeter).</p> <p>M. C.P. Butane container.</p> <p>N. Stop watch and timing mechanism</p> <p>O. Starting lever.</p> <p>P. Cord supply.</p> |
|---|---|

Quintuplicate specimens, 2 by 6 inches, are cut from the fabric being tested, 5 being cut parallel to the warp threads and 5 parallel to the filling. These are dried in an oven for 15 minutes at 105° C. and cooled in a desiccator for at least 3 minutes. The desiccator contains anhydrous cal-

cium chloride along with cobalt chloride to indicate the efficiency of the desiccant. Specimens are tested immediately upon removal from the desiccator and the data recorded as to the time in seconds which elapses from the moment the flame contacts the fabric until the apex of the flame reaches a plane horizontal to the top edge of the specimen. Bringing the starting lever over to the extreme right and releasing it starts the timing mechanism which applies the flame to the fabric for the 1-second period of exposure. The timing is automatically recorded by the watch, starting when the flame first contacts the specimen and stopping when the flame reaches and burns the fine thread across the top of the specimen.

Just what flaming time is to be considered as the demarkation line between acceptable and dangerous fabrics will necessarily be dependent upon the outcome of the extensive correlations now in progress.

b. Tests for Relative Combustibility

Still considering treated fabrics which are flame resistant but do not possess sufficient flame retardancy to prevent combustion once ignition has been accomplished, tests have been developed to determine the relative burning rates of fabrics. This type of test is a valuable tool in the more fundamental studies of flameproofing agents. It enables one to make close comparisons between the relative efficiencies of various treatments by studying the burning characteristics of low add-on fabrics. The sensitivity of the test is such that the effect of sizing alone on the burning rate of the fabric may be clearly indicated.

Flame-Rate Test. This test for measuring the rate of flame propagation of a burning fabric was developed in the course of the experimental work of the flameproofing project at Columbia University under N R C Project Q.M.C. #27. No special apparatus is required for carrying out the test though a convenient cabinet could easily be designed.

A 2 by 30 inch strip of the fabric to be tested is marked off in 5-inch intervals and suspended from a wire by means of small metal clips placed at 2.5-inch intervals along the entire length of the specimen. The wire is held taut at an angle of 30° to the horizontal and the fabric surface lies in a vertical plane. The entire apparatus must be enclosed in a draft-proof hood. The fabric is well ignited at the lower end by means of a match or Bunsen burner and notation made of the time required for the flame to travel each 5-inch interval. The time is not recorded for the first interval since burning begins erratically and becomes steady during this period. Similarly, the time for the last 5-inch interval is not very dependable since the burning often becomes erratic at the end of the strip. By plotting length in inches against time in seconds and taking the slope of the line, the burning rate of the fabric is expressed in terms of inches per second.

It is convenient to cut the test strips parallel to the filling threads though

specimens may be taken with warp or filling as long as they are cut consistently in the same direction of the fabric. In some cases where one surface of the cloth varies radically from the other, as with the brushed pile type of fabric, it is desirable to suspend the test specimen with the fabric surface in a horizontal plane. This is readily accomplished by supporting the strip between two parallel wires. A convenient method of attaching the fabric to the wires is by means of an office stapling machine. The wire staples are driven loosely into the edge of the strip such that one arm of the staple clamps into the fabric and the other arm remains free to be threaded on the supporting wire. The versatility of the test is enhanced by the ability to vary the angle of inclination of the test strip. When interested primarily in fabrics of very low combustibility the specimen may be inclined at an angle approaching the vertical. With highly combustible fabrics, on the other hand, the test strip may be inclined at angles only slightly removed from horizontal. Obviously, for any given set of comparative tests, the angle of inclination should be held constant.

Q.M.C. Flammability Test.⁴ This test as employed at the Philadelphia Quartermaster Depot requires a test specimen 1 by 6 inches.

The apparatus consists of two metal frames resembling miniature ladders which are hinged together at their upper ends and supported from a ring stand at an angle of 30° to the horizontal. The frames are 8 inches by 1.25 inches, the cross rods being 1.5-inch lengths of No. 28 heat-resistant wire.

The specimen is clamped between the two frames with 0.25 inch of the lower end hanging down from the frame end. Ignition is accomplished by holding a safety book match to this lower end for 5 seconds. Notation is made of the time required to burn the 6-inch strip including the 5-second ignition period. In the event that the specimen is not consumed, the length of the charred area is taken as the measure of "flammability." The results are expressed in the following manner:

"N" seconds or

"Supports combustion," extinguished after "N" seconds; "x" char length or

"Does not support combustion"; "x" char length.

This test does not provide the sensitive differentiation of the foregoing test but is convenient for some applications. In general the use of supporting wires across the test specimen introduces inconsistencies into the results due to the heat taken up by the wires themselves.

c. Tests for Relative Flameproofness

A great many different flame tests have been developed for determining the relative efficiencies of flameproofed fabrics. The tests differ from one

⁴"Test Methods for Textiles." P Q D. No. 447A (Jan. 10, 1945).

another with respect to the test cabinet, size of sample, alignment of the test specimen, nature of the heat source, duration of exposure of the heat to the fabric and the observations recorded. Some of the available tests are valuable for certain specific uses but are not generally applicable to the over-all problem of flameproofness. Others are almost universally applicable to the testing of flameproofed fabrics but do not emphasize one

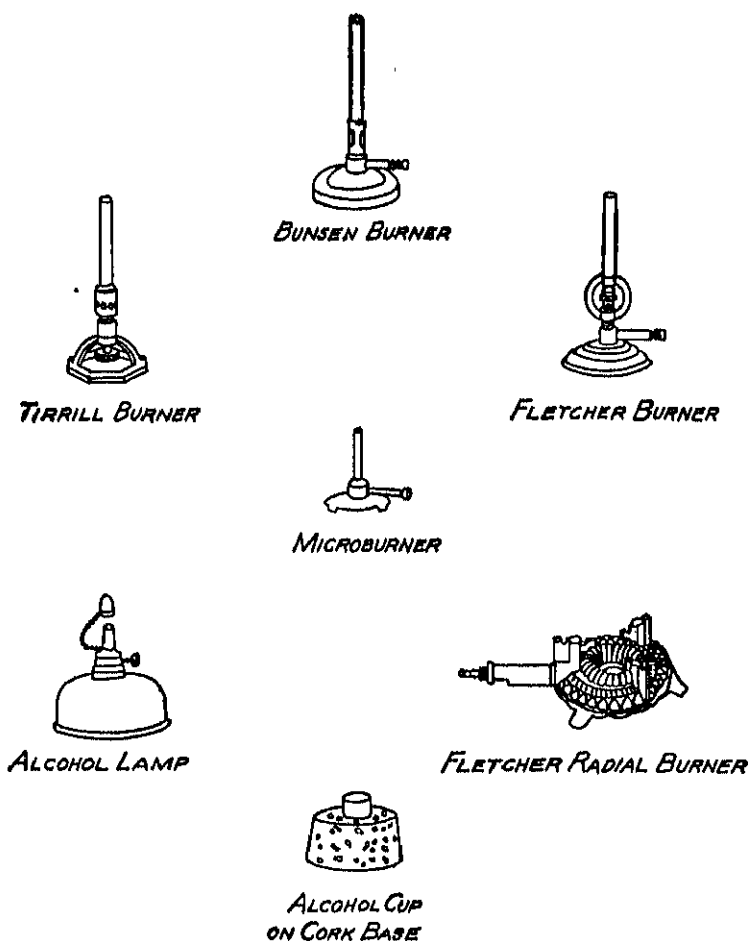


Figure 2. Various flame sources employed in tests for relative flameproofness

characteristic sufficiently to be desirable for very specific applications. A few of the better-known flame tests, which are representative of the several types, are presented in the following pages. A brief description of apparatus and technique has been given in each case. With the more or less standard tests the reader is referred to the literature cited for the details which have been omitted. To assist in describing the means of ignition

in the several tests, the more common flame sources are presented pictorially in Figure 2.

(1) *Vertical Specimens*

Underwriters' "Flammability" Test.⁵ The apparatus consists of a sheet iron stack, 12 inches square and 7 feet high which stands on legs 1 foot off the floor. The test specimen, which is 7 feet long by 5 inches wide, is hung from a bar at the top of the tube such that its bottom edge is 5.75 inches above the top of a 0.375-inch Fletcher burner. The burner flame is adjusted to a height of 11 inches by varying the air intake, maintaining a gas pressure of 108 mm. of water. The specimen is exposed to the flame for a 2-minute period and the time of ignition and time of cessation of flaming and glowing recorded. Also a measurement is made of the distance from the tip of the flame to the top of the charred area.

The test as described has several limitations. The test specimen is not held securely in place during the test and hence moves about as flaming progresses. The test is by necessity limited in its applicability as a research instrument because of the space required to house the apparatus and the amount of material required for the test specimens.

Freeman Stove Pipe Test.⁶ The apparatus in this case consists of a 5-inch brass tube, 24 inches long, which is lined with asbestos paper. The tube is ventilated by means of eight 0.75 by 1.50 inch vertical slots at the bottom. Six 24 by 3 inch specimens are tested simultaneously by hanging them at regular intervals from a rack at the top of the tube. Ignition is accomplished by burning 1 oz. of excelsior inside the base. Relative performance is based upon the per cent of the initial weight lost.

A modification of this test has also been proposed⁴ in which the igniting flame is that of a 5-inch radial Fletcher burner adjusted to a height of 4 inches. In the modified test only three specimens are tested at one time and the exposure time is reduced to 15 seconds.

Due to the severity of the conditions of this type of test, most flame-proofed fabrics are almost completely destroyed and thus there is little opportunity for differentiation between various treatments. In addition the deterioration in terms of per cent loss in weight depends too much upon the weight and weave of the fabric used.

Vertical-Bunsen Burner Test. The test cabinet consists of a sheet-metal shield 12 inches wide, 12 inches deep and 30 inches high, open at the top and provided with a vertical sliding glass door. A space is left at the bottom of the front to permit manipulation of the gas burner used in igniting the specimen.

⁵ "Recommended Requirements for Flameproofing of Textiles." Nat'l. Fire Protection Assoc., Boston, Mass. (1941).

⁶ *Trans. Am. Soc. Mech. Engr.*, 27, 71 (1906).

With each sample of flameproofed fabric, ten 2 by 12.5 inch specimens are cut for test, five with their long dimension in the direction of the warp and five in the direction of the filling. The specimen being tested is suspended vertically from the top of the cabinet by means of a clamp which covers the upper 0.5 inch of the length. The lower edge of the specimen is adjusted to be 0.75 inch above the top of a Bunsen or Tirrill gas burner. The burner has a tube of 0.375-inch inside diameter and the flame height is regulated to 1.5 inches with the air supply completely shut off. The resulting flame is luminous and wavering.

The flame is applied vertically in the middle of the lower end of the specimen for 12 seconds, then withdrawn and the duration of afterflaming, in seconds is noted. The specimen remains in place in the cabinet for the duration of any afterglow and the length of the charred portion is then measured. This is accomplished by inserting hooks in the lower portion of the specimen, one on each side of the charred area, supporting a given weight on one hook and slowly raising the other. The char length is defined as the distance from the lower edge of the specimen to the extremity of the tear produced.

The criteria of an effectively flameproofed fabric by this test are that the specimen shall not show more than 2 seconds' afterflaming, the average length of char of the ten specimens shall not exceed 3.5 inches, and the maximum length of char for any one specimen shall not be greater than 4.5 inches.

This test is quite widely used and, with minor differences, is the test employed by the U. S. Bureau of Standards,⁷ the National Fire Protection Association,⁸ U. S. Government Agencies,^{9, 10} American Society for Testing Materials,¹¹ and the National Research Council of Canada.¹² The cabinet specified by the Bureau of Standards is 14 inches wide rather than 12. As employed at the Philadelphia Quartermaster Depot, the apparatus includes a sample holder which clamps the specimen preventing curling and wavering during the test. In addition, the specimens are removed from the test cabinet when afterflaming has ceased and hung on a special wire rack throughout the afterglow period. Both the cabinet and the afterglow rack are kept in a draft-proof hood. The method and apparatus of the Canadian National Research Council differ from the above method in

⁷ "Flameproofing of Textiles" S. B. Detweiler, Jr.—Letter Circular No. 467—Nat'l. Bur. St'ds. (1936).

⁸ Duck, Cotton; Fire, Water and Weather Resistant Fed Spec CCC-1-746 (Feb. 17, 1939).

⁹ "Test Methods for Textiles." P.Q.D. No. 447A (Jan. 19, 1945).

¹⁰ Quartermaster Corps, Tent. Spec.—J.Q.D. No. 242 (Dec. 2, 1942).

¹¹ "Tentative Specifications for Fire-Retardant Properties of Treated Textile Fabrics." A.S.T.M. Standards on Textile Materials.

¹² "Schedule of Methods of Testing Textiles." Canadian Gov't. Purchasing Standards Comm.—No. 4-GP-2-1942 (Oct. 15, 1940). Amended Jan. 16, 1942.

two important particulars. The cabinet does not have a glass door on the front, both the top and front being open. Furthermore, in addition to the afterflaming time and char length, attention is paid to the occurrence of any flashing of the sample upon contact with the flame and the time of afterglow is measured.

The Vertical-Bunsen test possesses many advantages, among them being the simplicity of operation, small specimen required and the small flame which helps in attaining reproducibility. It also, however, suffers from several disadvantages, some of which can be obviated rather easily.

In the early work of the N.R.C.-Q.M.C. Flameproofing Project at Columbia University, a Flame Test Cabinet was developed in which vertical, horizontal and 45° flame tests could be carried out (see Figure 3). In adjusting the Vertical-Bunsen test to this cabinet as a research instrument for use on flame-proofed clothing fabrics, several of the previous disadvantages were avoided. A small pilot light was attached to the burner which provided instantaneous ignition and more accurate timing of the ignition period. Furthermore, it eliminated the necessity of moving the burner into position each time. The burner was fixed permanently in position in the cabinet which greatly improved reproducibility. As an additional aid in maintaining a constant adjustment of specimen and burner, the lower corners of the test strip were anchored to the floor of the cabinet by means of rubber bands or light wire springs. These could be easily clipped on the fabric and held it quite firmly in position without excess tension on the specimen. The cabinet itself was covered on top leaving a ventilation hood, and the opening at the front was replaced by a series of 0.5-inch holes along the bottom of each side. This provided adequate ventilation but avoided undesirable drafts. The extremely wavery luminous Bunsen flame necessitated reducing the open spaces in the cabinet in so far as possible. All test specimens were conditioned for at least 24 hours in the standard atmosphere of 70° F. and 65% R.H. and it is believed that this should be one of the required steps in all flame test procedures. Since the clothing fabrics being tested were generally efficiently flameproofed, the specimens were allowed to remain in the test cabinet throughout the afterglow period. This has been found to lead to more consistent and dependable data whether the actual time of afterglow is considered or not. In the belief that afterglow occurring in the clothing could be equally as dangerous as afterflaming and much more difficult to extinguish, the time of afterglow in seconds was observed along with the afterflaming time and length of char. The criteria of flameproofness assigned to the Columbia tests were that the treated fabric exhibit no afterflaming, less than 4 seconds' afterglow, and a char length not greater than 3.5 inches. These requirements as to the performance of the specimen in the flame test are obviously dependent upon the weight of the fabric, the type of treatment desired, and the use for which the fabric is intended.

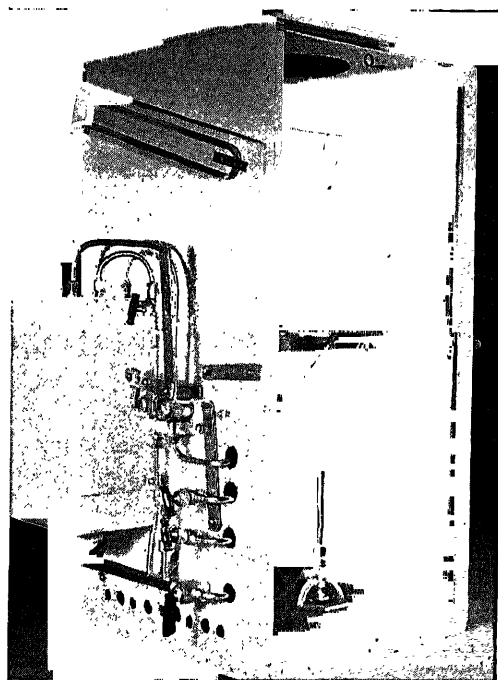
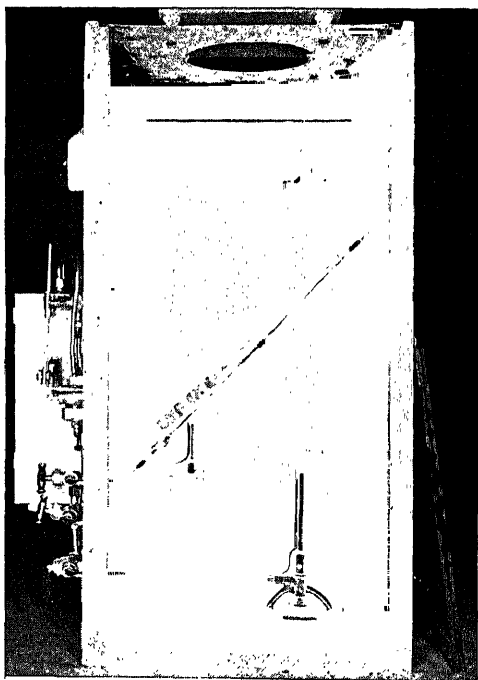
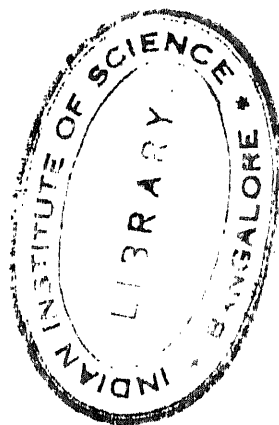


Figure 3. Columbia Flame Test Cabinet.

A. Side view, showing pyrex-glass doors in place, control valves and reservoir-manometer system for maintaining constant gas pressure.



B. Front view with sliding doors removed showing vertical and 45° test specimens in position for testing.



In comparison with 45° and horizontal tests, the alignment of the test specimen in the vertical direction produces those test conditions which are the most severe with respect to afterglow. Many treated fabrics which display no afterglow in the horizontal or 45° tests show a relatively strong afterglow when subjected to the vertical test. In contrast, the Vertical-Bunsen test shows the least tendency towards afterflaming when testing efficiently flameproofed fabrics. It is therefore apparent that, though it may have universal applicability, the Vertical-Bunsen burner flame test is of particular value in those cases where afterglow is the flameproof characteristic of primary interest.

(2) *Horizontal Specimens*

Corps of Engineers—"Flame-Resistance" Test.¹⁸ No specific test apparatus is described in the specification though it is stated that "the test shall be conducted in a hood or enclosed space so that the test shall not be affected by drafts."

Two 9 by 6 inch specimens of the impregnated fabric are conditioned for not less than 24 hours in the standard atmosphere and immediately tested. By means of a testing frame (which is not described) the specimen is supported in a horizontal position with the center of the specimen 3 inches above the lip of the cup containing the fuel. The igniting flame is obtained by burning 0.3 ml. of anhydrous ethyl alcohol (absolute) in a flat-bottomed brass cup. The brass cup is constructed of $\frac{1}{32}$ -inch sheet stock and is $1\frac{1}{16}$ inch in outside diameter and $\frac{9}{32}$ inch high. A material of low heat conductivity such as cork is used as a base for the test cup. The test specimen remains in position until afterglow has ceased. Without removing the specimen from the testing frame the charred area of the fabric is removed by punching a hole in the char and running a pencil around the inside of the hole with slight pressure on the sides. A measurement is then made of the longest dimension of the resulting hole. The requirement of flame resistance is that the average size of the burned hole shall not exceed 2.5 inches.

Apparently no attention is paid to the duration of either afterflaming or afterglow. The test was designed for a specific purpose and is limited in its applicability.

Horizontal-Microburner Test. In designing the cabinet for the testing of flameproofed fabrics under the Columbia University flameproofing project, a rack was designed which enabled the use of horizontal specimens and the microburner flame. In the photographs of the Columbia Flame Test Cabinet shown in Figure 3, the supporting strips for the horizontal rack can be seen along the sides of the cabinet in Figure 3-B.

¹⁸ Corps of Engineers, Tentative Specification—"Compound, Flame Resistant, Emulsifiable, for Fabrics." E.B.P. No. 674 (June 29, 1944).

Both the apparatus and test procedure for this test are identical with those of the 45°-Microburner test described in the following section, the only differences being the use of a different supporting rack to hold the specimen frame and the placing of the specimen such that the flame impinges on the center of the test piece.

Placing the specimen in a horizontal position produces test conditions which are the most severe with respect to afterflaming. The prevention of the removal of combustible decomposition products by any natural draft greatly intensifies the tendency of the fabric to flame after the igniting flame has been extinguished. In many instances fabrics which exhibit no afterflaming tendencies in the vertical and 45° tests show several seconds' afterflaming when tested horizontally. This test, therefore, is much more sensitive to minor differences in afterflaming tendencies and would be preferable for those applications where the flameproof characteristic of primary interest is the relative resistance of the treated fabrics to afterflaming. The tendency of fabrics to afterglow when tested horizontally is not nearly as great as in the case of the 45° and vertical tests. For this reason, in cases where the resistance to afterglow is felt to be of primary interest or equal in importance to the afterflaming tendencies, the horizontal test would be less desirable than one of the other two.

(3) 45° Specimens

British Standards Institution Test.¹⁴ The apparatus consists of a wire grid which is stretched on a 6.5-inch square metal frame and rested on vertical supports at an angle of 45 degrees. The igniting flame is produced by burning 0.3 ml. of absolute ethyl alcohol in a small metal cup. The cup is identical with that previously described under the horizontal test of the Corps of Engineers. In this case, the cup is supported on a cork such that the center of its base is 1 inch vertically below the center of the lower fabric surface.

A 6 by 6 inch specimen is spread over the wire grid and exposed to the alcohol flame which generally lasts for 45 to 50 seconds. A record is made of the afterflaming and afterglow times following the extinction of the igniting flame and the extent of the char is measured. The requirement for a well-treated fabric is that it shall not char for a length greater than 2 inches.

Canadian Surface Burning Test.¹² This is essentially an improved modification of the British Standards Institution Test. The apparatus and procedures are essentially the same as those described above with the following modifications:

The test specimen is 6 by 7 inches and is fastened to a metal frame such that a 6 by 6 inch surface is exposed. The sample is clamped at the

¹⁴ British Standards Specification 476 (1932).

four corners and is in contact with the metal frame on only two sides. The entire 6 by 6 inch square is open to the flame and is not in contact with a wire screen. Furthermore, the test is carried out in a three-sided sheet metal screen, 10 inches wide, 10 inches deep, and 32 inches high, thus affording some protection from drafts. Three specimens are cut from each sample to be tested and classified according to the afterflaming time, afterglow time, and char dimensions under one of the three following categories: non-inflammable materials, materials of very low inflammability, and materials of low inflammability. It should be noted here that afterglow which is confined to the charred area is disregarded in this test.

45°-Microburner Test. The Flame Test Cabinet developed by the personnel of N.R.C. Project Q.M.C. #27 at Columbia University is pictured in Figure 3. The wooden cabinet is 12 inches wide, 12 inches deep, and approximately 25 inches high by inside dimensions. The front of the cabinet is completely closed by means of two vertical-sliding pyrex glass doors. Ventilation is afforded by means of the 0.5-inch holes along the bottom of each side and the 6-inch hooded vent in the top. The microburner is securely fastened to a square wooden block which is set in a fixed position in the cabinet. Notched metal strips screwed to the sides of the cabinet serve to keep the specimen racks in constant alignment with the burner. Two sets of these strips are used, one to support the rack for the 45°-Microburner test and the other for the shorter rack of the horizontal test as described earlier in this section. The gas to be supplied to the microburner is held at a nearly constant pressure by means of the reservoir shown. The water manometer indicates the relative gas pressure and when at an angle of 15° to the horizontal is maintained at approximately 22 mm. A small pilot light is permanently attached to the microburner and avoids moving the heat source once the specimen is in position for test.

Three identical specimens are prepared for each measurement, being conditioned for at least 24 hours at 70° F./65% R.H. before testing. A 7 by 7 inch test specimen is placed smooth side up in a 5.5-inch square metal sample holder similar to an embroidery frame. The sample is placed at an angle of 45° in the metal rack which is positioned so that the lower part of the fabric directly above the microburner is 0.75 inch above the top of the burner. The center of the burner is 1 inch horizontally from the edge of the lower metal strip holding the sample. The microburner flame, previously adjusted with a slight yellow tip to a height of 1.75 inches by means of the needle valve in the gas supply line, is applied to the smooth side of the fabric near the lower edge for a period of 12 seconds. The specimen remains in position in the cabinet throughout the afterglow period. The data recorded include the duration of afterflaming and afterglow in seconds and the charred area as measured with a planimeter.

Investigation has shown that, for all practical purposes, it is immaterial

whether the flame burns in the direction of the warp threads, in the direction of the fill threads, or at 45° to both as shown in the illustrations. It has recently been found, however, that the charred area can be most consistently measured by tearing the charred portion similarly to the practice in the Vertical-Bunsen test. This is accomplished by cutting a small cross in the char directly above the burner and carefully tearing the char, once in the direction of the filling and once parallel to the warp threads, pulling against a standard weight hooked into the fabric. The torn charred area is then defined by connecting the four extremities of the tears using a soft red pencil and following the general shape of the total darkened area. When the torn charred area is to be measured, the specimen should be aligned in the cabinet so that the flame burns in the direction of either the warp or the filling.

The Columbia Test Cabinet incorporates several advantageous features which afford a simpler and more reproducible test procedure and also tend to give a greater degree of precision in flame test measurements. The addition of pilot lights avoids the use of matches or other methods of ignition and leads to more accurate timing of the ignition period. In addition, the sample and burner are in constant alignment which contributes greatly to the reproducibility of data. The closed cabinet is practically draftless and yet possesses good visibility and adequate ventilation to insure a good supply of air. The reservoir and manometer system on the gas-inlet line to the microburner could undoubtedly be improved upon but some similar measure should be taken to insure a fairly constant gas supply to the burner. The entire apparatus is compact and in one piece permitting it to be moved from one place to another without requiring extensive readjustment.

The microburner flame has many advantages over the luminous Bunsen flame. Being non-luminous, the flame of the microburner burns much more steadily and vigorously and is not affected by slight drafts. The Bunsen flame, in contrast, wavers with any air current and may be blown completely away from the test specimen by a moderate draft. The temperature of the microburner flame at the point of contact with the fabric is quite constant remaining at $823 \pm 11^\circ \text{C.}$ over a period of weeks. This will be dependent of course upon the uniformity of the particular gas supply used. The temperatures of the two flames are actually very similar at the point 0.75 inch above the top of the burner as illustrated in Figure 4.

It has been pointed out previously that the flame tests in which the specimen is aligned in a vertical position are the most severe with respect to afterglow. Similarly, placing the test specimen in a horizontal position tends to intensify the afterflaming tendency of the fabric. As might be expected, fabrics tested by means of a 45° test exhibit afterflaming tendencies midway between the vertical and horizontal tests and afterglow tendencies more severe than the horizontal test but not as extreme as when suspended vertically. Consequently, in choosing a flame test for universal

applicability, wherein the characteristics of afterflaming and afterglow are weighted equally in importance, it would be advisable to use the 45° compromise which does not exaggerate either the flaming or glowing tendencies. If, for a particular application, the resistance to afterflaming is the characteristic of major importance, the 45° test should be supplemented by measurements using the horizontal test. If the afterglow is of

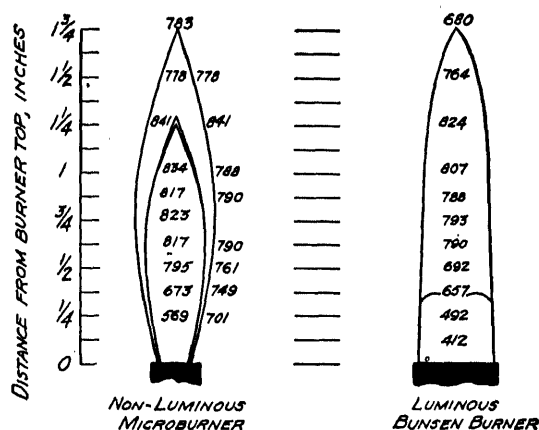


Figure 4. Comparative temperatures of Microburner and Bunsen burner flames as employed in standard flame tests.

major importance and the afterflaming a secondary requirement, the 45° test should be supplemented by parallel determinations with the vertical test. Regardless of the requirements to be met, considerable experimental data have clearly shown that the 45° test produces much better reproducibility and allows a wider differentiation between the relative efficiencies of comparable flameproofing treatments.

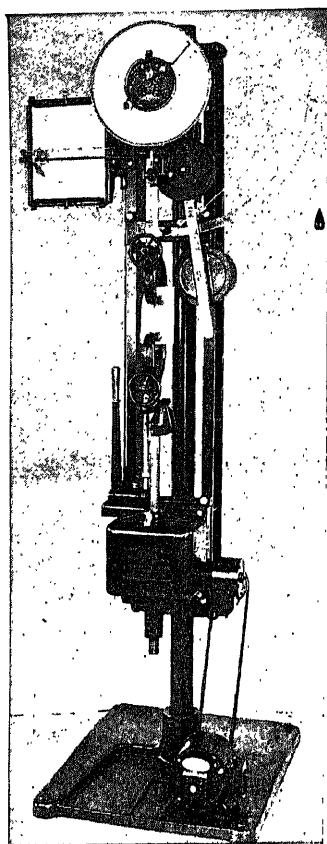
3. FABRIC STRENGTH

Robert W. Little

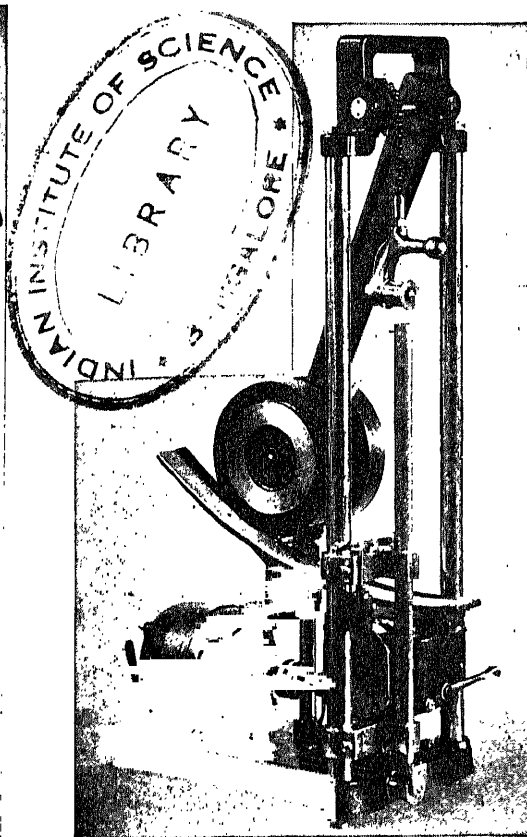
Of primary importance in the evaluation of a flameproofing treatment or flameproofed fabric is the measurement of the effect which the treatment has upon the strength characteristics of the cloth. A retardant treatment, regardless of its efficiency in the prevention of afterflaming and afterglow, would be quite unsatisfactory for any practical application if, in the course of the treatment or use of the treated fabric, the strength was seriously impaired so as to render the fabric unserviceable. For this reason, the tensile and tear strengths of the fabric are generally determined before and after the application of the flameproofing treatment and also after exposure of the treated material to surveillance and permanence tests.

The selection of a test apparatus and procedure to be employed is rela-

tively simple since these techniques for studying the load-elongation relationships of fabrics have been carefully standardized and universally accepted. The reader is referred to standard specifications of these tests



*Courtesy of Scott Testers, Inc.,
Providence, R. I.*



Courtesy of Alfred Suter, New York, N. Y.

Figure 5. Pendulum type tensile testing machines.

(left) Scott Model J showing fabric clamps and autographic recorder.

(right) Suter tester equipped with skein rollers. These may be replaced by fabric clamps and an autographic recorder can be attached.

for the details which may be omitted from the following discussions.^{15,16}

Of the two general types of textile testing machines for the determination of the breaking strength and elongation of textiles,¹⁷ i.e., the pendulum

¹⁵ A.S.T.M. Standards on Textile Materials (1944).

¹⁶ Textiles, General Specifications, Test Methods—Fed. St'd. Stock Catalog, Sect. IV, Part 5—CCC-T-191a (April, 1937).

¹⁷ Standard Specifications for Textile Testing Machines—A.S.T.M. Designation D76-42.

type and the constant specimen-rate-of-load type, the former is perhaps more widely used and will be considered in this discussion. Typical examples of the industrial machines available are the Scott and Suter Testers shown in Figure 5. Several different models of this type of instrument are available, varying in capacity and design, in many cases having been developed for a specific fiber or fabric.

The strength characteristics of a fabric which are of major interest are the breaking strength, the elongation and the tear strength.

a. Breaking Strength

Grab Method. The distance between the clamps at the start of the test is exactly 3 inches. The face of one jaw is 1 by 1 inch square and that of the other jaw 1 by 2 inches or more, with the longer dimension perpendicular to the direction of application of the load.

The test specimens are cut 4 inches in width and not less than 6 inches in length. Quintuplicate specimens are used for determining warp breaking strength which have the longer dimension parallel to the warp yarns. An equal number are cut with the longer dimension parallel to the filling threads for determining the filling strength.

The specimens are placed symmetrically in the clamps with the longer dimension parallel to the direction of application of the load, care being taken to see that the same yarns are gripped in both clamps. The average of the five individual specimens shall be reported as the warp or filling breaking strength. Individual results which fall appreciably below the average are discarded as are the results of tests in which a jaw break or slippage is apparent.

Raveled-Strip Method. With the following exceptions, this test is carried out in the same manner as described for the grab test:

The faces of the jaws, in this case, measure 1 by 1.5 inches or more, the longer dimension being perpendicular to the direction of application of the load. Test specimens are cut 1.25 or 1.5 inches in width, depending upon the number of threads per inch, and raveled to a width of exactly 1 inch by removing approximately the same number of threads from each side.

Cut-Strip Method. This test is performed just as described for the Raveled-Strip test with the exception that the specimens are cut to a width of 1 inch rather than cutting wider and raveling to that width. The test is applicable to those coated or impregnated fabrics which would be difficult or impossible to ravel.

b. Elongation

Using testing machines as described above, which include an autographic recording device, the elongation of the fabric can be determined

at the same time that the breaking strength measurement is made. The elongation at any stated load can be obtained from the graph and the average of the five specimens expressed as elongation in terms of percentage increase in length.

c. Tearing Strength

Tongue Method. Using the same machine as described for the method for breaking strength, the pawls of the pendulum are disengaged from the ratchet.

Quintuplicate specimens, 3 inches in width and at least 8 inches in length, are cut in both the warp and filling directions. A 3-inch longitudinal cut is made from the center of one of the short edges and running lengthwise of the specimen. One of the tongues is placed in each clamp of the tester and, by means of the autographic recording device, a measurement made of the average load necessary to tear the fabric. The warp and filling tearing strengths are reported in the form of the average of the five individual tests.

Trapezoid Method. The machine is again the same as that used for the grab breaking strength measurement with the exceptions that the faces of the clamps are 1 by 3 inches or more, with the long dimension perpendicular to the direction of the load, and the distance between the clamps at the start of the test is 1 inch. Again, the pawls of the pendulum are disengaged from the ratchet.

Quintuplicate specimens, 3 inches in width and 6 inches in length, are cut in the directions of both warp and filling threads. An isosceles trapezoid is marked on each specimen having an altitude of 3 inches and bases 1 and 4 inches in length. A 0.25-inch cut is made in the center of the 1-inch edge and perpendicular to it. The specimen is clamped in the machine along the non-parallel sides of the trapezoid with the cut halfway between the clamps, the short edge taut and the long edge lying in folds. The average load necessary to tear the fabric is obtained by means of the autographic recording device. The warp tearing strength and filling tearing strength are calculated as the average of the five individual tests in each case.

The various types of flameproofing treatments exert quite different effects upon the strength characteristics of the fabric. In some cases the breaking strength is seriously impaired with only a relatively slight decrease in tear strength. Those treatments which tend to produce a film or coating on the fabric, on the other hand, do not reduce the breaking strength but generally cause a marked decrease in tearing strength. Which of the fabric strength measurements assumes the greatest importance depends to an appreciable extent upon the future use for which the treated fabric is intended.

4. LEACHING TESTS

*Rogers B. Finch, Allan J. McQuade,
and Robert W. Little*

a. Laboratory Tests

In the development work on flameproofing treatments of a more or less durable nature, it is often desirable to employ a rapid and simple laboratory test to obtain an initial estimate of the permanence of the treatment. In the event that the flameproofing constituents withstand these mild leaching conditions they may then be considered of a durable type and evaluated further by means of the more severe laundering and sea water tests which follow.

Static Water Leach. A 7 by 7 inch specimen of the treated fabric is conditioned for 24 hours at 70° F. and 65% R.H. and weighed. It is then sewn to a 6 by 6 inch rectangular stirrer frame made of glass rod and immersed in approximately 4 liters of distilled water in a 4-liter beaker. The stirrer is rotated for 1 hour at room temperature at a rate of approximately 40 R.P.M. After removal from the beaker and frame, the specimen is air-dried, reconditioned in the standard atmosphere and re-weighed to determine any loss of retardant. The specimen is finally tested by means of the 45°-Microburner flame test.

This mild leaching is concerned with removal by a dissolving action only since the use of distilled water avoids any possible exchange and the slow stirring exerts almost no mechanical flexing on the fabric.

Running Water Leach. Two methods used in evaluating fire-resistant treated fabrics are described in this section. The first method was developed for use under N.R.C. Project Q.M.C. #27 at Columbia University. A 7 by 7 inch specimen of the fabric is conditioned and weighed. It is then immersed in a round-bottomed trough of approximately 1-gallon capacity into which tap water is introduced at such a rate as to produce marked turbulence. The water is introduced at the bottom of the tank and exits at the top, producing a tumbling action. The specimen is tumbled in this running water for a period of 24 hours, air-dried and reconditioned. The fabric is then weighed to determine the loss of flameproofing agent and its flameproofness checked with the 45°-Microburner Test.

The exposure of some treatments to such large quantities of tap water will produce some loss of flameproofness due to ion-exchange. This will vary with the hardness of water used. In addition, the mechanical action occurring in the tumbling of the specimen may cause some impairment of retardancy though this should not be appreciable.

The second method is used at the Jeffersonville Quartermaster Depot for the leaching of fire-resistant duck for tentage. There, in order to

accommodate the large number of samples received daily for both inspection and development purposes, a tank 42 inches in length, 19 inches wide, and 21 inches deep is employed. This tank is divided lengthwise into three parts to produce along each side a compartment 2 inches wide parallel to the length. The center portion, 15 by 42 inches, is further partitioned across its length into 40 cells approximately 1 inch in width, thus providing a separate compartment for each sample to be tested and avoiding the possibility of contamination. Water is piped to the center of the tank and enters one of the narrow sections parallel to the length of the tank. By means of slots the flow of water is then directed to the top of each sample compartment. At the bottom of each compartment and on the opposite side from the inlet the water is directed into the third section which runs parallel to the length of the tank. A waste pipe is placed in the center of this section at a level slightly below that of the inlet to draw off the flow of water. The inflow water pipe is jacketed to allow it to be heated by steam, the introduction of which is thermostatically controlled to insure water of 70° F. temperature.

Thus this leaching tank provides a means for a constant flow of water of even temperature to be directed down and across each sample which hangs vertically in an individual compartment free from contamination of materials removed from other samples.

In the conduct of the test two fabric samples each 12.5 by 10 inches in size are selected, one with the longer dimension parallel to the warp and the other parallel to the filling. Each is suspended below the water level in separate compartments, and the water flow is regulated to provide at least six complete changes of water during each 24-hour period. Upon completion of the desired leaching period, generally for 72- or 168-hour periods, the fabric samples are removed and air-dried before exposure to standard conditions. Each sample is then cut into five 2.5 by 10 inch specimens to allow fire-resistance determinations to be made using the Vertical-Bunsen test.

On the whole, fair results were experienced with this method and those fabrics which had water-soluble fire retardants were quickly discovered. In addition, when fabrics leached for 168 hours in this tank were examined for mildew resistance the results gave a good indication of the mildew resistance of the same fabric after 4 to 6 months' outdoor exposure in Jeffersonville.

Spray Leaching. Leaching of fire-resistant tentage fabrics at Jeffersonville was also carried out in a Model X-1A Accelerated Weathering Unit manufactured by the National Carbon Company.¹⁸ In this machine a circular rack 37.5 inches in diameter revolves within an enclosed drum at such a speed as to provide one complete revolution for each two-hour

¹⁸ For details of the equipment and operating procedure, see paragraphs 5b and 5b(2), Section IV, U. S. Army Spec. No. 100-48 (May 11, 1945); also see Section 9 of this chapter.

period of machine operation. Located within the revolving rack a spray nozzle is provided to impinge water in a conical spray upon samples carried by the revolving rack. In the center of the machine is a carbon arc enclosed with Corex D filter panels. To provide artificial light, Sunshine type carbons are employed and maintained at constant amperage across the arc. Thus, during each revolution the samples are exposed to the spray for approximately a ten-minute period, and the remaining time to light. The period of exposure to such conditions is generally 200 hours, and for some comparative tests it has been extended to 400 and 600 hours.

In the conduct of the test two fabric samples each 12.5 by 11 inches in size are selected, one with the 11-inch dimension parallel to the warp and the other sample with its 11-inch length parallel to the filling. The samples are positioned upon the revolving rack with the 11-inch dimension in a vertical plane and are attached solely to its top portion. Upon completion of the desired exposure period, the fabric samples are removed and air-dried for a 24-hour period before exposure to standard conditions. The unexposed portion of the sample, 1 by 12.5 inches in size, is removed and the remaining fabric divided into five specimens each 2.5 by 10 inches. These are used for fire-resistance tests employing the Vertical-Bunsen method. It was also the practice to apply the flame to that 2.5-inch edge which had been in the lowest position during the test.

This test method provides a much better indication of the fire-resistance retention of tentage duck than did the tank method previously outlined, and in addition a fair estimation of the color change to result in field tests is obtained. However, in both these respects it is not as severe as that which occurred in field tests. As would be expected where a large quantity of tap water of considerable hardness is employed, one type of finish was markedly impaired due to ion-exchange reactions. Such a condition has not been fully confirmed upon actual outdoor leaching.

b. Field Tests

Outdoor exposure of tentage fabrics is performed on the grounds of the Jeffersonville Quartermaster Depot with the sample mounted at a 45° angle, facing south.¹⁹ A specimen 42 by 30 inches with its longer dimension parallel to the warp is mounted on fiber board using large copper tacks spaced 6 inches apart. In some cases the fabric is supported on all four sides, providing no backing agent. In this manner one side is exposed to the weather for periods up to one year.

In nearly all instances the fabric samples were mounted on the fiber board since this produced a more severe condition and the tensile strength losses sustained were more in keeping with those experienced in other localities. In addition, it represented a use comparable to that which occurred in the life of paulins.

¹⁹ Paragraph 3, Section XIII, Federal Spec. CCC-T-191a (April 23, 1937).

Due to the fact that Jeffersonville is located in an atmosphere in which industrial gases prevail, especially during the winter months, it was necessary that only those exposures which were initiated about April 1 and continuing for a six months' period be considered as somewhat indicative of the effectiveness of the treatment. Lastly, to allow comparison between various types of treatments it became necessary to standardize on two types of base grey fabric, which were 12.29-ounce Army duck and 11.6-ounce tent twill.

The significance of these tests in comparison with laboratory evaluations is discussed in Chapter VII, Section A-2-b.

5. LAUNDERING TESTS

Robert W. Little

Since the durable types of flameproofing treatments are intended for an initial treatment without the necessity of reprocessing, they must be capable of withstanding normal laundering conditions. A test procedure is required, therefore, to evaluate in the laboratory the resistance of flameproofed fabrics to laundering. The retention of flame and glow resistance on laundering will be greatly dependent upon the washing procedure employed and the nature of the detergent solution. For this reason it is necessary to adhere to a more or less empirical test method in order to achieve any degree of reproducibility.

Several standard laundering tests have been developed for determining the color fastness of dyed fabrics. The official methods of the United States Government,²⁰ the American Association of Textile Chemists and Colorists,²¹ and the American Society for Testing Materials²² are very similar in nature and with minor modifications are applicable for use in testing the permanence of flameproofed fabrics. In the case of the color fastness tests, several separate procedures are given using different constituents in the wash solution and varying bath temperatures and the length of the washing period. In adapting the techniques for use with flame-retardant fabrics a single washing procedure was employed, the severity of the laundering being varied only with respect to the detergent mixture employed.

A second type of laundering test which could be used for the evaluation of flameproofed fabrics is that now commonly employed in determining shrinkage in laundering.^{20,23} This method employs a large specimen, 20

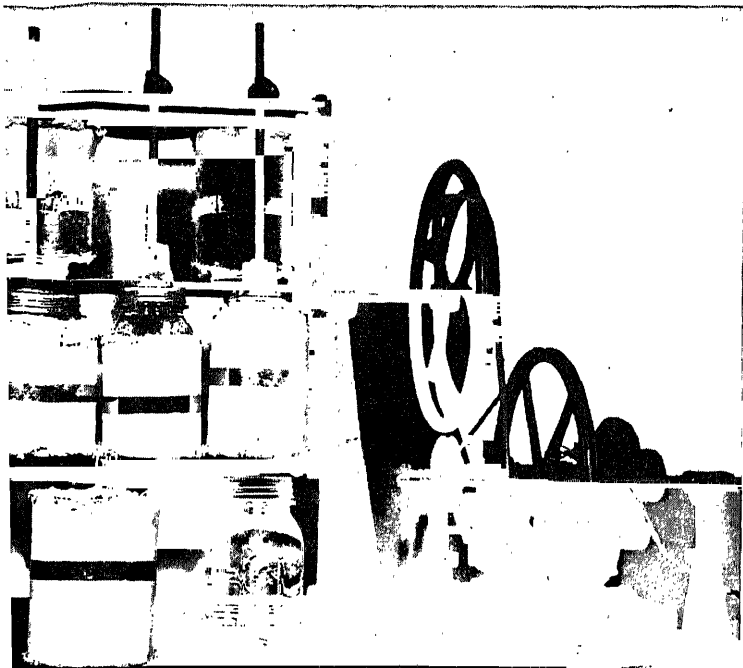
²⁰ Paragraph XIII-4, Textiles, General Specifications, Test Methods—Fed. St'd. Stock Catalog, Sect. IV, Part 5—CCC-T-191a (April, 1937).

²¹ A.A.T.C.C. Official Method C-1-42 (No. 3)—Standard A.A.T.C.C. Test Methods, 1943 Yearbook.

²² A.S.T.M. Designation: D435-42 (No. 3); A.S.T.M. Standards on Textile Materials (1944).

²³ A.S.T.M. Designation D437-36; A.S.T.M. Standards on Textile Materials (1944).

3 or larger, and the washing is carried out in a small reversing of the cylindrical type. A test of this sort might more nearly be the conditions existing in commercial laundry practices. Laboratory comparisons of the relative permanence of flameproofing however, where it is often desirable to test several different simultaneously, the first mentioned tests appear to be better. The individual specimen jars permit the washing of many different specimens without any chance of contaminating one fabric products leached from another.



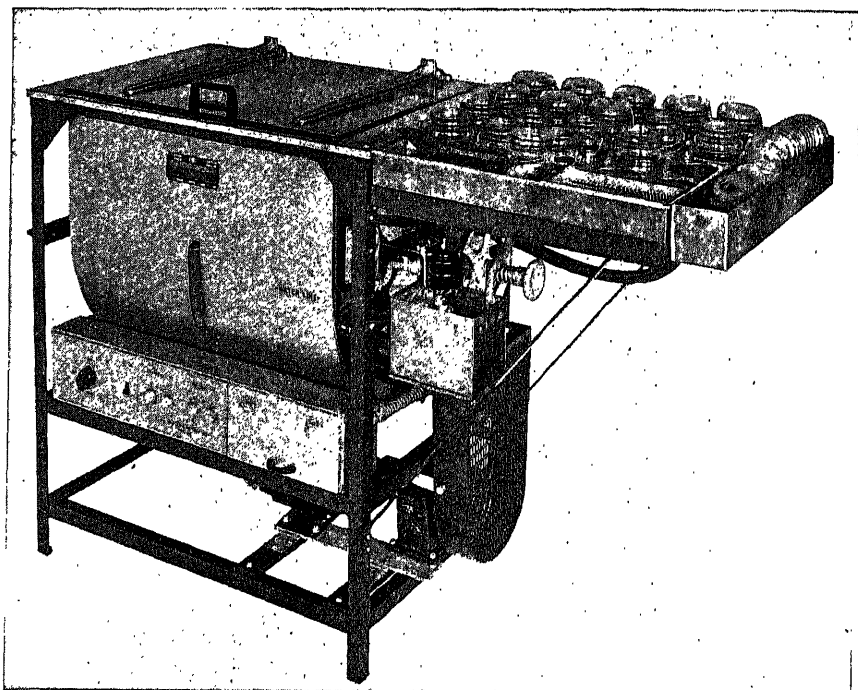
laboratory rotator employed as a launderometer in the early experiments of N.R.C. Project Q.M.C. #27.

ering tests carried out in the course of the flameproofing Columbia University were performed in two types of launderometer. One washing procedure was developed making use of a rotator which would accommodate jars of one-quart capacity. Series of tests were carried out in the A.A.T.C.C. standard rotator. The apparatus and procedure of both tests are presented on the following pages in order to be of assistance to those who may not have a Launder-Ometer available but do have a laboratory rotator adapted to accommodate one-quart jars.

7. **Launderometer.** The complete apparatus employed is shown in Figure 6. The rotator consists of a cast iron frame capable of

holding six 1-quart Mason jars. The jars are clamped, three on each side of the frame, such that the jars on opposite sides are also at the opposite ends of the rotating holder. The horizontal shaft of the machine is 0.5 inch above the plane of the jar cap and is displaced 2 inches from the vertical axis of the jar. Thus the jars in revolving effectively rotate about an axis approximately 2 inches above the center of their covers. The Mason jars are encased in asbestos jackets and clamped in the rotator which turns at the rate of 15 R.P.M.

The procedure used is very similar to that described in Federal Specifications.²⁰ A single specimen is placed in a 1-quart Mason-type jar along



Courtesy of Atlas Electric Devices Co., Chicago, Ill.

Figure 7. Atlas Launder-Ometer, Model LHD-BF.

with twenty 0.75-inch glass marbles. 400 cc. of the soap solution, which has been heated to 160° F., is added to the preheated jar, the jar sealed and rotated for 30 minutes. The soap solution is then poured off, replaced by 400 cc. of water at 160° F., and the jar rotated for 10 minutes. The specimen is rinsed once more by rotating for 10 minutes in a fresh 400-cc. portion of water at 160° F., and finally by rinses of 3 minutes each in an 0.05% acetic acid solution at room temperature, and in cold water. The rinsed specimen is hung to dry under room conditions.

Atlas Launder-Ometer. The fully automatic, electrically operated machine, including the preheated loading table, is shown in Figure 7.

A detailed description of the apparatus and the process of its development can be obtained from the literature.²⁴ The use of a specially designed instrument of this type has many advantages particularly when a great number of tests are being made. The automatic temperature regulation of the bath and preheating table plus the compactness and ready availability of the items required reduces greatly the tedium of routine tests. The machine consists essentially of a large copper tank containing a rotor capable of holding twenty standard pint jars. The rotor is driven at a standard speed of 42 R.P.M. The jars, covers, rubbers and test balls are all preheated to the operating temperature in the tray shown by means of circulating the water from the laundering chamber.

The laundering procedure in this case is very similar to that of test No. 3 of A.S.T.M.²² and A.A.T.C.C.²¹ A single test specimen is placed in a 1-pint Mason-type jar along with ten 0.25-inch steel balls. A 100-cc. portion of soap solution, previously heated to 160° F., is added and the jar rotated for 45 minutes at that temperature. The soap solution is then poured off and the specimen subjected to two consecutive 1-minute rinses in 100 cc. of water at 105° F. The fabric is then soured by agitating for 2 minutes in 100 cc. of 0.05% acetic acid solution at room temperature followed by a 2-minute rinse in 100 cc. of cold water. The rinsed specimen is hung to dry under room conditions.

The A.A.T.C.C. launderometer can be obtained with a special rotor to accommodate 1-quart jars. This is desirable in view of the size of specimen required for the 45°-Microburner flame test. In that case the volumes of solutions used would be increased to those given for the laboratory launderometer method.

In the laundering tests carried out under the N.R.C.-Q.M.C. Flameproofing Project, three different soap solutions were employed:

Solution 1 — 0.5% Igepon-T.

Solution 2 — 0.5% ordinary issue G.I. soap.

Solution 3 — 0.5% G.I. soap + 0.2% Na_2CO_3 .

These were intended to represent the varying degrees of severity which might be encountered in the course of military or commercial launderings. Since the launderings are intended primarily for use in comparative studies it is not necessary to duplicate exactly all of the conditions which may be encountered in actual usage.

Although the two techniques described above are quite different in several respects, extensive laboratory comparisons have shown that they are nearly equal in their effect upon the flameproof characteristics of the fabrics tested. This is illustrated by the data of Table 1, comparing the flameproofness of three different fabrics after laundering according to both

²⁴ *Am. Dyestuff Rep.*, p. 697 (Oct. 29, 1928).

procedures. The figures in the table represent the average of from 9 to separate specimens.

Table 1. Comparison of Laundering Techniques: Flameproofed Fabrics Laundered 0.5% G.I. Soap Using a Laboratory Launderometer and the Atlas Launder-Ometer

Treatment	Launderometer	No. of Launderings	AF secs.	AG secs.	CA, in ² CL, in
<i>45°-Microburner Flame Test</i>					
Urea-Phosphate	—	0	0	2	2.2
Type	Atlas	3	0	2	2.6
(Lab.)	"	6	0	1	2.2
(12.3% add-on)	Lab.	3	0	3	2.2
	"	6	0	3	2.0
Urea-Phosphate	—	0	0	1	2.1
Type	Atlas	3	0	2	2.2
(Comm'l.)	"	6	0	3	2.9
(23.9% add-on)	Lab.	3	0	3	2.3
	"	6	0	1	2.7
Antimony Oxide:	—	0	0	0	2.4
Vynlite (Solvent	Atlas	3	0	0	2.5
(Semi-comm'l.)	"	6	0	0	2.0
(38.5% add-on)	Lab.	3	0	0	2.3
	"	6	0	0	2.1
<i>Vertical-Bunsen Burner Flame Test</i>					
Urea-Phosphate	—	0	0	2	3.4
Type	Atlas	3	0	2	3.6
(Lab.)	Lab.	3	0	3	3.2
(10.1% add-on)					
Urea-Phosphate	—	0	0	1	2.5
Type	Atlas	3	0	2	2.5
(Comm'l.)	"	6	0	2	2.7
(23.9% add-on)	Lab.	3	0	3	3.2
	"	6	0	3	3.2
Antimony Oxide:	—	0	0	20	3.7
Vynlite (Solvent)	Atlas	3	0	31	3.2
(Semi-comm'l.)	"	6	0	66	3.6
(38.5% add-on)	Lab.	3	0	32	3.2
	"	6	0	35	2.9
AF — afterflaming		CA — charred area			
AG — afterglow		CL — charred length			

6. SEA WATER RESISTANCE

Robert W. Little

The resistance of durable flameproofing treatments to the leaching action of sea water is a property which probably is most directly associated with fabrics for Naval and military purposes. The test was nec-

sary in evaluating military clothing fabrics which might well be exposed to more or less prolonged immersion in sea water in the course of amphibious landing operations. It is also probable, moreover, that flameproofed duck used for tarpaulins or deck covers might well be exposed to a similar leaching action on exposure to sea air and spray. The test is more universal, however, since it is concerned with the resistance of flameproofing compositions to an exchange reaction with alkali and alkaline-earth ions whether brought about by sea water immersion, saturation with perspiration or leaching or laundering in hard water. The treatments primarily concerned with these base exchange reactions are those of the urea-phosphate type. The influence exerted by alkali and alkaline-earth ions upon the salts of cellulose esters has been previously discussed. The pigment-type emulsion and suspension treatments are not seriously affected by sea water immersion though in some cases the resistance to afterglow is somewhat impaired.

In the course of the experimental work of the Flameproofing Project at Columbia University, it was necessary to develop an apparatus and procedure for carrying out this test. The only available comparable tests, those commonly employed in estimating the fastness of dyes to perspiration and sea water, were entirely unsuitable for the purpose.

The apparatus consists of a standard laboratory rotator in which cylindrical, wide-mouthed jars of 1-pint capacity are rotated at a speed of approximately 12 R.P.M. about an axis parallel to the diameter of the jars.

The synthetic "ocean water" is prepared in the form of two stock solutions and diluted for use as required. The compositions of the stock solutions, according to the formulae of Lyman and Fleming,²⁵ are as follows:

<i>Stock Solution #1</i>		<i>Stock Solution #2</i>	
<i>Material</i>	<i>Grams</i>	<i>Material</i>	<i>Grams</i>
NaCl	1878.	MgCl ₂ · 6 H ₂ O	851.9
Na ₂ SO ₄	313.4	CaCl ₂	88.2
KCl	53.1	SiCl ₂ · 6 H ₂ O	3.2
NaHCO ₃	15.4	H ₂ O	800.
KBr	7.7		
H ₃ BO ₃	2.1		
NaF	0.24		
Na ₂ SiO ₃ (40%)	3.4		
H ₂ O	7000.		

A volume of 195 cc. of solution #1 is diluted with water to a total volume of 1 liter. Similarly, 35 cc. of solution #2 is diluted up to 1 liter with water. The two liters are then mixed and the resulting solution used in the tests.

²⁵ "The Oceans," Sverdrup, Johnson, and Fleming, Prentice Hall, Inc. (1943).

Six identical specimens of fabric, 7 by 7 inches square, are cut for test. A specimen is placed in each of the jars along with 250 cc. of water" and rotated for the required time at 70° F. The specimen is removed from the jar, blotted between cotton toweling to remove excess solution, and air-dried. After conditioning the specimens for at least 24 hours at 70° F. and 65% R.H., they are tested for flameproofness by means of the 45°-Microburner flame test.

One specimen of the group, in each case, is subjected to rotation in sea water for a period of 15, 30, 60, 90 and 120 minutes. The sixth specimen is tested as a control. The results are expressed in terms of "Resistance to Sea Water," which may be defined as the time in minutes which a flameproofed fabric may be rotated in the "ocean water" solution without significantly affecting the flameproof qualities of that fabric. In the case of military clothing fabrics it was required that the resistance to sea water be at least 120 minutes.

7. PERSPIRATION RESISTANCE

Robert W. Little

The measurement of the resistance of flameproofed fabrics to the action of perspiration is a test intended specifically for use with clothing fabrics. The property evaluated is similar to that determined by means of the Water Resistance Test previously described but the latter is considered more severe in its leaching action.

The most satisfactory method of determining the deleterious action of perspiration upon flameproofed clothing fabrics would naturally be a series of heat load experiments in which the treated garments are actually exposed to the sweat of human subjects under controlled wearing conditions. Experiments of this type have been conducted and the method used will be discussed in a later section. In the majority of cases, however, it is either impractical or impossible to carry out extensive programs of this type. It is therefore desirable to develop a simple accelerated laboratory test which approximates as closely as possible the conditions encountered by the fabric in the course of the heat load experiments.

The only available tests for determining the resistance of textiles to perspiration were those employed in measuring the fastness of dyes under conditions of those tests were thought to be too mild for the purpose in mind. The test procedure which follows was developed by the staff of the Flameproofing Project at Columbia University in an attempt to provide a simple laboratory test which would simulate the life of a garment fabric under severe wearing conditions.

The test apparatus presented diagrammatically in Figure 8 consists of a closed cabinet with a glass front which is maintained at a temperature approximating that of the body (30° C.). The fabric specimens are

pended on a wire frame which may be slowly rotated. The synthetic perspiration solution is introduced into the cabinet in the form of a very fine spray by means of an air-powered spray gun.

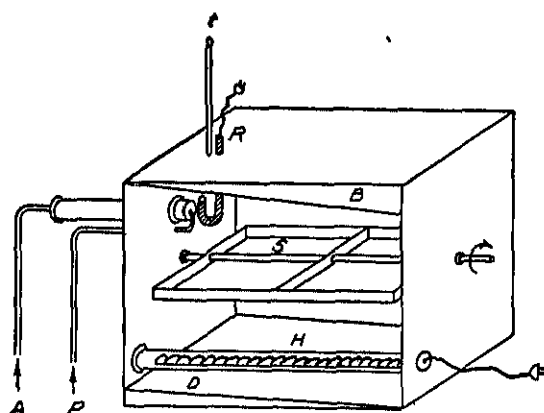


Figure 8. Perspiration-spray cabinet.

A - Air
P - Perspiration Solution
H - Heater
D - Drain Board
S - Specimen Holder
R - Thermo-regulator
t - Thermometer
B - Baffle

The synthetic "perspiration" is prepared according to the following formulation:²⁰

Acid Perspiration Solution

<i>Material</i>	<i>Grams</i>
Sodium chloride	10
Lactic acid, U.S.P. (85%)	1
Disodium orthophosphate	1
Water	988

Duplicate or quadruplicate 7 by 7 inch specimens are placed in the cabinet for an 8-hour period, being sprayed intermittently at 1-hour intervals with 30 cc. of the perspiration solution. The specimens are finally conditioned for 24 hours in the standard atmosphere and tested for flame-proofness using the 45°-Microburner flame test.

In the testing of water-soluble flameproofing agents, the spray should be adjusted such that the specimens do not become oversaturated and cause dripping of solution from the fabric. Actually, extensive practical wear tests have shown that water-soluble retardants can be effectively leached from the fabric by profuse perspiration.

²⁰ Federal Standard Stock Catalog—Section IV, Part 5, p. 15. CCC-T-191a. (Apr 23, 1937.)

8. MOISTURE VAPOR PERMEABILITY

Robert W. Little

One of the requirements for flameproofed fabrics intended for use articles of clothing is that the fabric shall allow a free passage of wa vapor in order that an excessive heat load is not imposed upon the wea of the garment. The most reliable method of determining this fabric pr erty would be to carry out heat load studies and observe the performan of the fabric when in actual use on human subjects. This type of expe ment has been carried out on flameproofed fabrics and is described in Section 10 of this chapter. Since such extensive experiments are genera impractical it is desirable to have a simple laboratory test which v serve to evaluate the resistance of the fabric to the passage of moist vapor.

A great many different methods have been developed for testing vapor permeability of fabrics, paper, leather and various sheets and fil The reader is referred to the literature for a detailed picture of the pro dures^{27,28,29,30,31,32} and apparatus^{33,34} employed. A bibliographical summa of the available methods has recently been presented by the staff of The Institute of Paper Chemistry.³⁵ In general the tests consist of a method of measuring the rate at which water vapor passes through a sheet from a region of high humidity to one of lower moisture vapor co tent. The method of Lyman Fournet and Milton Harris of the Textile Fou dation³⁶ relates this passage of water vapor to the intrinsic resistance of the fabric. The intrinsic resistance, expressed in terms of equivalent ce timeters of still air, is determined for a fabric before and after the a plication of a flame-retardant material, thus determining whether or n the flameproofing treatment has impaired the passage of water va through the cloth.

The majority of the vapor permeability techniques measure the to resistance set up by a fabric system. This includes the appreciable s tances of the air layers on each side of the fabric which are very c

²⁷ Hyden, W. L., *Ind. Eng. Chem.*, 21, No. 5, 405 (1929).

²⁸ John, R., *Tech. Assoc. Papers*, 20, 90 (1937).

²⁹ Holwech, W., *Papir J.*, 20, 233 (1932).

³⁰ Hobbs, R. B., *J. Am. Leather Chem. Assoc.*, 36, 346 (1941).

³¹ Herfeld, H., *Collegium*, 65 (1941).

³² Sears, G. R., Schlagenhauf, H. A., Given, J. C., and Yett, F. R., *Paper Trade J.*, 118, No. 3, 39 (1944).

³³ Noll, A., *Papier-Fabr. Wochbl. Papier fabr.*, No. 5, 151 (1944).

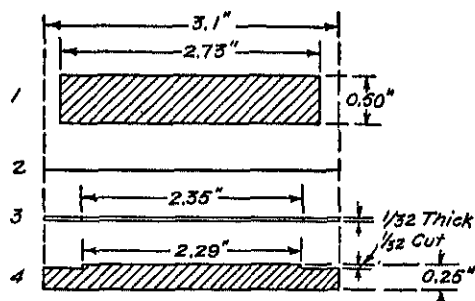
³⁴ *Modern Packaging*, 16, 78 (1942).

³⁵ *Paper Trade J.*, 121, No. 16, 33 (Oct. 18, 1945).

³⁶ Report No. 243, Committee on Aviation Medicine, N.R.C. Div. of Med. (Jan. 7, 1944).

pendent upon the conditions of test. By comparing the total resistances of two systems, one of which contains one more layer of fabric than the other, the intrinsic resistance, or the resistance attributable to the fabric alone, may be obtained. This technique of Fourn and Harris was felt to be more applicable to fabrics and is presented here as one of the better methods available.

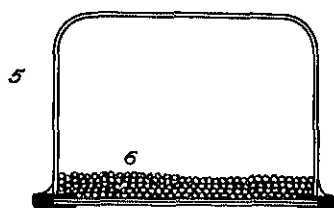
The apparatus required consists of the parts illustrated in Figure 9 along with a suitable conditioning box or conditioning room in which the



PARTS FOR ASSEMBLY

- 1 Steel sealing disc
- 2 Fabric disc
- 3 Aluminum ring
- 4 Steel jig
- 5 Crystallizing dish
- 6 Drierite

Figure 9. Moisture vapor permeability apparatus.



3 Layer Assembly Ready for Test

assemblies may be exposed to an atmosphere of high and constant humidity. As employed in the experimental program of the Columbia University Flameproofing project, the assemblies were placed on a wire screen suspended in the conditioning room. Since the fabric specimens are conditioned in this standard atmosphere of 70° F. and 65% R.H. prior to test, this avoids any pickup of moisture on the part of the fabric in the early stages of the test.

Nine circles of fabric, 3.1 inches in diameter, are cut using one of the aluminum rings as a pattern. These provide specimens for a vapor permeability measurement on 1, 3 and 5 layers of the fabric. The specimens

should be taken from various parts of the cloth sample to minimize error due to non-homogeneous treatment.

The steel sealing disc and a cup of sealing wax are kept on a hot plate throughout the preparation of the assemblies. A satisfactory sealing wax may be made of a 50-50 mixture of paraffin and beeswax. An aluminum ring is placed on the jig and the outer half of the upper surface painted with sealing wax. A corresponding circle of wax is painted around the edge of one surface of a fabric specimen, the cloth disc placed on the ring with the two waxed surfaces together and the two sealed together by placing the hot sealing disc on top of the fabric. For the 1-layer assembly, this procedure is repeated sealing a second aluminum ring on the other side of the fabric. In the case of the 3- and 5-layer assemblies, the adjacent cloth discs are sealed together as described above, placing a ring of sealing wax on both discs, pressing them carefully together and sealing with the hot steel disc. In each case the last cloth layer is topped with an aluminum ring. Finally, the edges of the completed assemblies are painted with wax to assure an airtight seal, and the three assemblies conditioned for 24 hours at 70° F. and 65% R.H. Twenty grams of Drierite are placed in each of three tanning dishes, a fabric assembly placed on each dish and sealed in place with sealing wax. The final assemblies are placed fabric side down on a large-mesh wire platform which is in the conditioning room. A uniform current of the moist air passes steadily over the surface of the exposed fabric. The entire assemblies are weighed on an analytical balance at 30-minute intervals over a period of 2.5 hours. Just after each weighing the desiccant is mixed by gently shaking the dish.

Resistance being the reciprocal of permeability, a convenient unit for expressing the resistance of a fabric has been selected as the length of an equivalent column of still air through which water vapor would diffuse at the same rate under the same conditions of temperature, pressure and concentration gradient. The total resistance of a system, then, would be expressible in the following form:

$$R = \frac{1}{Q} D(\Delta C) A t$$

where:

- R = total resistance of the system, the resistance to the diffusion of water vapor expressed in equivalent centimeters of ideal still air.
- Q = mass of water transferred by diffusion, in grams.
- D = diffusion constant in cm^2/sec .
- ΔC = difference in concentration of water vapor in gms/cm^3 .
- A = area of fabric through which moisture travels in cm^2 .
- t = time interval, in seconds.

In order to clarify the calculation of test results, a sample calculation is given in the following section for a measurement of 8.5 oz. herringbone twill in a room at 70° F. (21.1° C.) and 65% R.H.

According to International Critical Tables, the diffusion coefficient, D , varies with the absolute temperature, T , and the barometric pressure, P (mm. Hg) as expressed in the equation:

$$D = 0.220 \left(\frac{T}{273} \right)^{1.75} \times \frac{760}{P}$$

As an approximation between 0 and 50° C., this may be replaced by:

$$D = 0.22 + 0.00147(m^\circ \text{C.})$$

Since the temperature in this case was 70° F. or 21.1° C.:

$$D = 0.22 + 0.00147(21.1) = 0.251 \text{ cm}^2/\text{sec.}$$

The concentration difference, ΔC , in grams/cm³, can be obtained from the relative humidities H_1 and H_2 , the absolute temperatures T_1 and T_2 , and the corresponding saturation vapor pressures p_1 and p_2 on each side of the fabric as:

$$\Delta C = \frac{MW_{\text{H}_2\text{O}}}{G.M.V.} \times \frac{273}{760} \left(\frac{p_1 H_1}{T_1} - \frac{p_2 H_2}{T_2} \right)$$

Since, however, the temperature and pressure both inside and outside are the same and the concentration of water vapor on the inside is essentially zero:

$$T_1 = T_2 = 273 + 21.1 = 294.2^\circ \text{K}$$

$$p_1 = p_2 = \text{saturation vapor pressure at } 21.1^\circ \text{C} = 18.76 \text{ mm.}$$

$$H_1 - H_2 = \text{difference in relative humidity from one side of the fabric to the other} \\ = 0.65 - 0 = 0.65$$

$$MW_{\text{H}_2\text{O}} = 18$$

$$G.M.V. = 22,400 \text{ cc under standard conditions and:}$$

$$\Delta C = \frac{18}{22,400} \times \frac{p}{760} \times \frac{273}{T} (H_1 - H_2) = \frac{18}{22,400} \times \frac{18.76}{760} \times \frac{273}{294.2} \times 0.65 \\ = 1.198 \times 10^{-5} \text{ gm./cm}^3$$

Also, since the exposed fabric disc has a diameter of 2.35 inches and the area is to be expressed in cm²:

$$A = \left(\frac{2.35 \times 2.54}{2} \right)^2 \times 3.1416 = 28.00 \text{ cm}^2$$

finally:

$$t = 60 M, \text{ where } M = \text{time interval in minutes between successive weighings}$$

Thus substituting in the original equation:

$$R = \frac{M}{Q} \times 0.251 \times 1.198 \times 10^{-5} \times 28 \times 60$$

or:

$$R = 5.05 \times 10^{-3} \frac{M}{Q}$$

Q is obtained by differences in successive weighings and along with time elapsed in minutes is then used in the above equation to calculate the total resistance R .

The data for the sample calculation are as follows:

No. of Layers of Cloth	Time	Wt. of Assembly, gms.	Q	M
1	2 : 08 P.M.	69.3009	—	—
1	2 : 40 P.M.	69.4432	0.1363	32
1	3 : 10 P.M.	69.5853	0.1421	30
1	3 : 40 P.M.	69.7115	0.1262	30
1	4 : 12 P.M.	69.8218	0.1103	32
Ave.				
3	2 : 27 P.M.	70.1872	—	—
3	2 : 57 P.M.	70.2843	0.0071	30
3	3 : 27 P.M.	—	—	—
3	3 : 57 P.M.	70.4977	0.2134	60
3	4 : 27 P.M.	70.5973	0.0906	30
Ave.				
5	2 : 19 P.M.	83.1336	—	—
5	2 : 47 P.M.	83.2082	0.0746	28
5	3 : 17 P.M.	83.2009	0.0887	30
5	3 : 47 P.M.	83.3780	0.0820	30
5	4 : 17 P.M.	83.4694	0.0905	30
Ave.				

The intrinsic resistance of one layer of fabric is obtained as follows:

$$R_1 \text{ layer} = \frac{R_2 \text{ layers} - R_1 \text{ layer}}{2} = \frac{R_3 \text{ layers} - R_2 \text{ layers}}{2}$$

also:

$$R_1 \text{ layer} = \frac{R_5 \text{ layers} - R_1 \text{ layer}}{4}$$

By these subtractions we cancel out the effect of the surface layer air on both sides of the cloth as well as the effect of the Drierite on side.

Using the sample data:

$$R_1 = \frac{1.50 - 1.24}{2} = \frac{0.26}{2} = 0.130 \text{ cm.}$$

$$R_1 = \frac{1.75 - 1.50}{2} = \frac{0.25}{2} = 0.125 \text{ cm.}$$

$$R_1 = \frac{1.75 - 1.24}{4} = \frac{0.51}{4} = 0.127 \text{ cm.}$$

Therefore, the intrinsic resistance of 8.5 oz. herringbone twill is 0 cm. The precision of the measurement is approximately ± 0.05 although this factor will depend greatly upon the allowed variation in relative humidity.

9. SURVEILLANCE AND TENDERING TESTS

Henry A. Rutherford and Robert W. Little

The application of a finish or a coating to a cotton textile frequently raises the question of whether the treatment has an adverse effect on the useful life of the material. Thus, many laboratory methods of ascertaining the stability of a fabric toward light, heat, moisture, mildew, etc., have been devised. These accelerated methods are desirable because of the impracticality of drawn-out and laborious service testing, but unfortunately they are often a completely inadequate substitute.

The conditions used in any of the so-called tendering tests are necessarily arbitrary, but are designed to bring into play those factors which are expected to contribute to the deterioration of the material during use. For example, the stability of a fabric during normal storage conditions might be ascertained by its behavior at some elevated temperature. Materials whose normal use constitutes exposure to the elements must be tested by a more complicated means involving the use of heat, light, and moisture. The reliability of the evaluation procedures is of utmost importance, and it may be said that the more drastic the conditions of accelerated testing, the greater the possibility of arriving at a false evaluation of the durability of a fabric during normal use.

The lack of standard test procedures emphasizes the difficulties involved in this type of work. A survey of the literature, which for the most part consists of government specifications, reveals a number of surveillance and tendering tests. Changes in details of procedure have been made from time to time, but in every case the general form of subjecting fabrics to heat, light and/or moisture separately or together has been followed. A description of accepted (but not necessarily proved) procedures in force in May, 1945, which might possibly apply to fire-resistant fabrics, is presented.

U. S. Army Specification No. 100-48, dated May 11, 1945, pages 35 and 36, lists the following:³⁷

"4. Accelerated aging tests.—

"4a *Oxygen bomb test*.—The given specimen of coated fabric shall be exposed to an atmosphere of oxygen at a pressure of 300 pounds per square inch and a temperature of 158° F. (70° C.) for a specified period of time. After exposure, the coating on the fabric shall show no signs of becoming stiff and brittle, nor soft and tacky, nor shall the loss in tensile

³⁷ Other references to tendering tests are as follows: Yearbook of the American Association of Textile Chemists and Colorists, A.S.T.M. Standards on Textile Materials; Federal Specification CCC-D-746; Q.M.C. Tentative Specification JQD 242; and U. S. Army Specification 6-345. These specifications are not necessarily in force.

strength, as determined by the grab method, exceed a specified per cent of the original tensile strength.

"4b. *Aging test, 100° C., 48 hours.*—The treated material shall be stored in an oven at a temperature of 100° C. for 48 hours and the resulting pH determined in the specified manner.

"4c. *Aging test, 175° F., 5 days.*—The sample of the treated material shall be placed loosely inside a quart Mason jar. The open jar containing the specimen shall be exposed to standard atmospheric conditions for 24 hours. At the end of the 24-hour period the quart jar shall be closed airtight, and then subjected to a temperature of $175^{\circ} \pm 5^{\circ}$ F. for 5 days. The breaking strength of the material shall then be determined.

"5. *Resistance to accelerated weathering.*—

"5a. *Test specimen.*—A sample of specified dimensions, with the long dimension in the direction of the filling shall be clamped to the inside rotating rack of the accelerated weathering test machine and exposed to the conditions described below.

"5b. *Accelerated weathering test machines.*—One of the following types of commercial machines as specified shall be used.

"5b (1). *Accelerated weathering machine.*—Atlas Electric Devices Company Model DL-TS. This double carbon arc apparatus shall be operated at ambient temperature as specified, and in accordance with the directions furnished by the manufacturer. The light and water spray shall be adjusted to provide light continuously and water intermittently in a constant cycle of 17 minutes without water and 3 minutes with water. The water shall be discharged at the rate of 0.5 gallon per minute and the drum shall rotate at the rate of 1 revolution per minute.

"5b (2). *Accelerated weathering unit.*—The apparatus shall consist of a vertical carbon arc mounted at the center of a vertical cylinder. The arc is designed to accommodate two pairs of carbons, No. 22, upper carbons, and No. 13, lower carbons; however, the arc burns between only one pair of carbons at a time. The arc shall be surrounded by panels of Correx D glass or other enclosure having equivalent absorbing or transmitting properties. The glass shall be cleaned at least once every 24 hours of operating time. The arc shall be operated on 60 amperes and 50 volts across the arc for alternating current of 50 amperes and 60 volts across the arc for direct current. The specimens for test shall be mounted on a rotating rack inside the cylinder and facing the arc. The diameter of the rotating rack shall be such that the distance from the center of the arc to the face of the specimen is $18\frac{3}{4}$ inches. The rack shall rotate about the arc at a uniform speed of about 1 revolution in 2 hours. Spray nozzles shall be mounted in the tank so that the specimens shall be exposed to wetting once during each revolution of the rack. An X-1A National Carbon weathering unit burning National Sunshine cored and copper-coated carbons will fulfill the above.

"5b (3). *Single arc accelerated weathering machine.*—The apparatus shall consist of a vertical carbon arc mounted at the center of a vertical metal cylinder. The arc shall be enclosed in a clear globe of No. 9200 PX Pyrex glass 0.0625 inch thick or other inclosure having equivalent absorbing and transmitting properties. The globe shall be cleaned when the carbons are changed or at least once every 36 hours of operating time. The arc shall be operated on 13-ampere direct or 17-ampere 60-cycle alternating current with the voltage of the arc 140 volts. The specimens for test shall be mounted on the inside of the cylinder facing the arc. The diameter of the cylinder shall be such that the distance of the face of the specimens from the center of the arc is $14\frac{3}{4}$ inches. The cylinder shall rotate about the arc at a uniform speed of approximately three revolutions per hour. A water spray shall strike each 2-inch-wide specimen in turn for about 1 minute during each revolution of the cylinder. An Atlas Electric Devices Co. single-arc weather-o-meter will fulfill the above conditions."

It must be emphasized again that these tests do not necessarily *predict* the behavior of flameproof fabrics during actual use, and that their primary function is to serve as a means of detecting materials or coatings which, under certain conditions, might have adverse effects on the fabric. They are also useful in ascertaining the effects of one treatment relative to another. For example, it has been observed that cotton duck, treated so as to be fire, water, weather, and mildew resistant, which contains an unstable chlorinated paraffin, exhibits an increase in acidity (decreased pH) during heating at 100° C., whereas one which contains a stable type material shows no change in this respect. Increase in acidity may be regarded as undesirable because of the sensitivity of cellulose to acids.

In most instances, the resistance of the fabric to aging is determined by loss in strength, but it is difficult to establish satisfactory levels of performance. Other tests, such as tearing strength and fluidity, are sometimes useful. The latter is of value in detecting certain types of incipient damage in cellulose which is not always revealed in losses in strength (see oxidation of cellulose). As a general rule, flameproof fabrics are also required to maintain their initial properties of flameproofness during exposure under the conditions of the various tendering tests.

At the outbreak of World War II, considerable impetus was given to the problem of evaluation of textiles by tendering tests. One of the most important items for consideration was duck, cotton; fire, water, weather and mildew resistant, because of its wide use in tentage and tarpaulins. The results of three years' work⁸⁸ showed that it was impossible to evaluate the potential life of fabrics of this type by any one of a number of accelerated laboratory tests. This is because the performance during natural weathering is largely dependent upon the location of exposure. In other words, no precise and fixed behavior of a fabric could be estab-

⁸⁸ Sponsored by the Office of the Quartermaster General

lished. Thus, it was made clear that the potential serviceability of fabrics for tentage can be reliably judged only by subjecting them to extensive exposure, and that the service life will depend upon the conditions prevailing at the point of usage.

Evaluation of duck, cotton; fire, water, weather, and mildew resistance under U. S. Army Specification 6-345 is based primarily on performance during exterior weathering in Yuma, Arizona, and New Orleans, Louisiana for a period of six months, April through September being preferred. These locations were chosen on the basis of their wide divergence in climatic conditions. The results of exposures made in desert areas lack the complication introduced by the action of microorganisms. Exposures in tropical or tropical areas have the primary function of establishing resistance of fabrics to mildew in the presence of sunlight and rain and ordinarily do not subject fabrics to the stringent conditions of high light intensity at low moisture levels.

In the course of the experimental work carried out under N.J. Project Q.M.C. #27 at Columbia University several surveillance and deriding tests were employed in order to anticipate the relative behavior of various flameproofed fabrics in the course of normal service. Comparative data were desired after long-term exposure under normal ambient conditions and also following short exposures to the extremes of temperature and humidity. As mentioned above, it was highly desirable that accelerated conditions should not be so severe as to cause chemical or physical changes in the flameproofing agent which would not also occur in time under the conditions of actual usage. The four test conditions selected, which will be briefly discussed in the following pages, are: (1) prolonged indoor storage under existing conditions, (2) extended outdoor exposure under prevailing weather conditions, (3) accelerated storage for 2, 3 and 4 weeks at 150° F., and (4) accelerated indoor storage for 2 weeks at 120° F. and 85% R.H.

Indoor Storage. Due to several experiences with the loss of effectiveness of certain water-soluble retardants on prolonged indoor storage, a surveillance procedure was adopted for a study of the temporary flameproofing agents. The testing procedure consists simply of suspending treated fabric samples in a closed room for long periods of time, removing test specimens at weekly or monthly intervals and testing for flameproofness or fabric strength after conditioning for at least 24 hours in standard atmosphere. Care should be taken that there are no folds or creases in the stored samples since it has been found that contact between fabric surfaces interferes with the vaporization or sublimation of volatile constituents. Since in a surveillance test of this type the existing conditions are extremely variable, it is well to conduct all experiments on a comparative basis referring to a standard fabric which is subjected to the same test period. The temperatures and humidities encountered

naturally vary greatly from one part of the country to another. The tests at Columbia were performed during the summer and fall months, the temperature ranging from 65 to 95° F. under nearly all possible values of relative humidity.

Outdoor Exposure. In a study of durable flameproofing treatments it is desirable to know the effect of outdoor weathering upon the permanence of the flameproofness and the properties of fabric strength. The procedure consists of stretching large samples of treated fabric on a metal frame and placing the frame in such a manner that the samples are completely exposed to wind, rain and sunlight. The supporting frames in this instance were supported at an angle of 45° facing the southeast, and the samples exposed to typical East Coast fall weather. In this case also it is essential that all data which are to be subsequently compared be collected in parallel tests under the same existing conditions. If this is not possible, the use of a standard reference fabric will permit some qualitative comparisons.

Accelerated Dry Storage. Flameproofed fabrics employed in articles of military clothing might well be exposed to long periods of storage prior to issue for use. It is imperative that during the storage period the garment does not undergo any serious impairment of its strength or flameproof characteristics. In an attempt to simulate the severe dry storage conditions which might be encountered in arid regions, a tendering test was employed wherein fabrics were exposed to a temperature of 150° F. for 2-, 3- and 4-week periods.

The tendering chamber consists of a large, triple wall, forced circulation oven in which the temperature can be controlled to $\pm 1^\circ$ F.

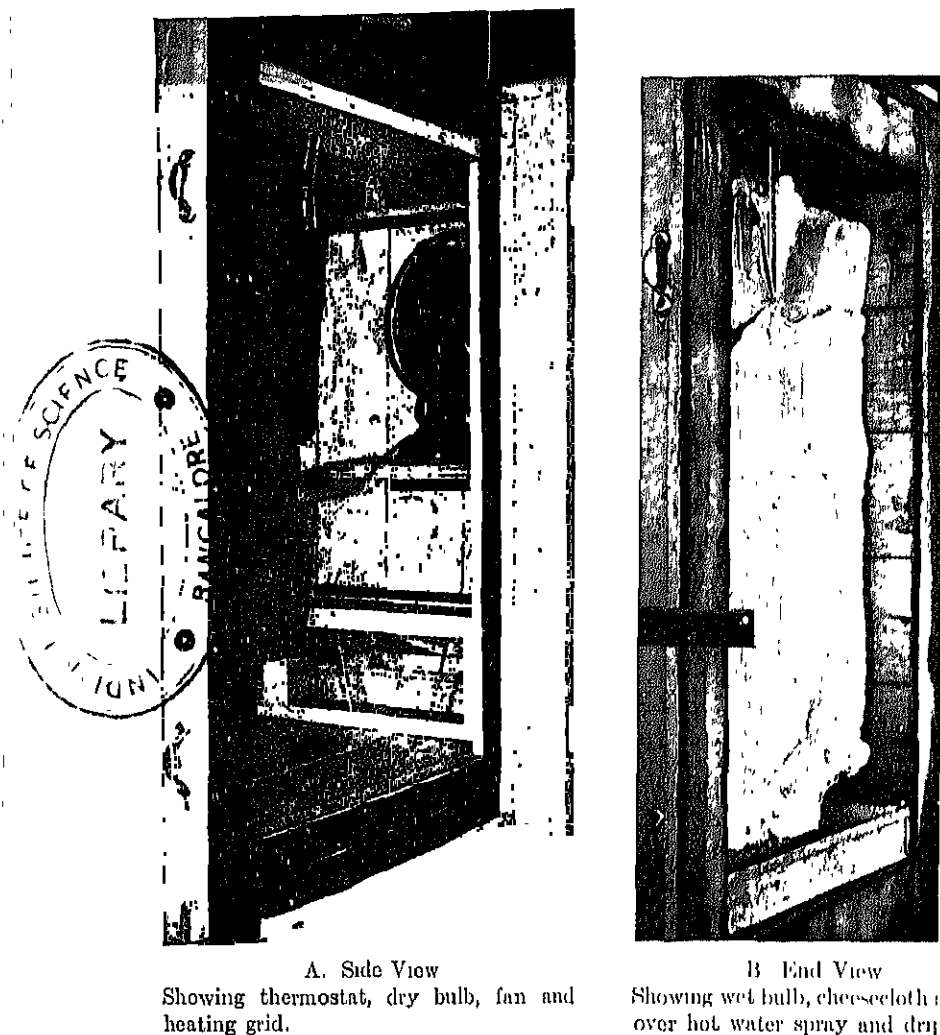
Samples of the treated fabric are suspended in the oven vertically, specimens being withdrawn at the end of 2, 3 and 4 weeks. In each case the specimens are reconditioned for at least 24 hours at 70° F. and 65% R.H., reweighed to determine possible loss in add-on and subjected to the tensile or flameproofness test.

Accelerated Humid Storage. In an attempt to simulate humid storage under severe tropical and jungle conditions tendering tests were also carried out for a period of 2 weeks at 120° F. and 85% R.H.

The tendering cabinet in this case was specially constructed for the purpose and is shown in Figure 10. The 4-inch walls contain 2 inches of rock-wool insulation and the doors are sealed by padding with a layer of felt around the jambs. Heating is accomplished by means of a nichrome electric grid heater regulated by means of a gas-mercury thermostat and suitable temperature regulator relay. The cabinet temperature can be maintained to $\pm 0.5^\circ$ F. The humidification system consists of a large cheesecloth screen continually wetted by a stream of hot running water. The air in the cabinet is circulated through the wet screen by means of a small electric fan. The relative humidity is constant to $\pm 3\%$.

The test procedure employed is essentially as described for the accelerated dry storage test.

As has been previously pointed out these accelerated tendering are valuable in the study of flameproofed fabrics in spite of the fact



A. Side View

Showing thermostat, dry bulb, fan and heating grid.

B. End View

Showing wet bulb, cheesecloth over hot water spray and drying grid.

Figure 10. Humid tendering cabinet.

they may not exactly predict the performance of the fabric under normal conditions of usage. They serve particularly well in comparing the performances of several differently treated materials, as is often desired in development work and furthermore are of great value as screening procedures. The ability to closely duplicate the conditions allows correlation

between experiments which may have been conducted over a very wide interval of time. This is a definite advantage over long-term exposure tests under existing weather conditions where all data which are to be considered comparatively must be obtained concurrently. The interpretation of results of either laboratory or field tests is unfortunately not a routine matter, and the limits or tolerances allowed in the various procedures described herein cannot be fixed. These limits are usually based upon personal judgment and experience, taking into account the conditions of the test.

10. PHYSIOLOGICAL HEAT LOAD EXPERIMENTS

William R. Christensen

Experiences of the past few years have clearly demonstrated that physiological heat load must be considered in the selection of uniforms for military personnel operating in tropical or desert terrain. It is essential that those uniforms which seriously interfere with the dissipation of bodily heat be avoided under such circumstances. If such garments are issued, they are likely to be discarded as soon as the heat becomes excessive (and their protective qualities thereby effectively eliminated) or, if retained, the incidence of heat exhaustion may be increased. An evaluation of the physiological heat load of military garments is, therefore, advisable or even essential.

Accurate accomplishment of this task requires considerable care and time. Very special types of equipment and a large number of trained, co-operative subjects are necessary. However, its value is manifest. In this section an attempt is made to present a simple but adequate test technique. The method described is based largely on the experiences of the Climatic Research Laboratory. This presentation is in no way intended to be comprehensive.

Fundamentally, all approaches to this problem are based on consideration of the human body as a heat-producing machine. The importance of imposed physiological heat load stems from the fact that the body temperature must be regulated within very close limits if operating efficiency is to be maintained. When exposed to low ambient temperatures, the human maintains a satisfactory mean temperature by certain physiological adjustments and through the addition of clothing, the thermal insulation of which reduces the loss of heat. At high ambient temperatures, the body must lose more heat or its temperature will mount and physiological breakdown will eventually occur. This heat is principally dissipated through radiation, conduction, convection, and evaporation. In any given case, the relative magnitude of the loss through each of these avenues is determined solely by the existing ambient conditions, *i.e.*, dry bulb temperature, intensity of solar and terrestrial radiation, air movement and

wet bulb temperature. Obviously, the most immediate effect of an excessive load upon the cooling mechanisms of the body would be a rise in the average temperature of the tissue mass. This is reflected by an increase in the skin and rectal temperatures. Concomitantly the cardiac output is increased, the most obvious sign being an increase in pulse rate, and peripheral vasodilation occurs. Sensible perspiration appears and increases roughly in proportion to the elevation of skin temperature. The majority of these responses can be interpreted as attempts to increase amount of heat loss. Their relative efficiency differs widely according to the exact conditions of wet and dry bulb temperature, radiation, and air movement. However, it is quite apparent that clothing of any type would act as a deterrent to the efficient dissipation of heat. The thermal insulation it provides reduces conductive losses when the ambient temperature is below that of the body surface. Convective cooling currents are largely eliminated because free circulation of air is prevented by the clothing. Garments also provide a radiation barrier. And, because they present a barrier to the diffusion of water vapor, evaporative heat loss is reduced. Under most circumstances of high temperature and humidity, therefore, clothing can be considered to constitute a barrier to heat dissipation by the body. As outlined above, the physiological effects which may be expected are an increase in rectal temperature, skin temperature, blood volume, cardiac output, pulse rate, peripheral blood flow, oxygen consumption and sweat production. If such trends are allowed to continue, efficiency is soon reduced and irreversible changes may ensue. Obviously the immediate solution is to discard all clothing. Many peoples living under conditions imposing heavy heat loads have come to this solution. However, the unacclimated soldier from temperate areas requires the protection against solar radiation, insects, skin trauma, etc., which a garment provides. Likewise if there are no garments there can be little or no protection against flame.

It is entirely logical to assume that the magnitude of the responses to heat would be directly related to the magnitude of the heat load imposed. This has been proved experimentally for a majority of these values. Therefore, by exposing human subjects in various garments to controlled conditions, an evaluation of the heat load imposed by the garments may be obtained from the magnitude of the physiological changes which they induce. Some of the physiological changes, however, can be more readily adapted to testing techniques than others. Determination of blood flow and oxygen consumption is too difficult for routine use. Changes in blood volume probably do not appear rapidly enough. Because of this, most investigators have depended upon measurement of skin temperature, rectal temperature, pulse rate, and sweat production for evaluation of garments. The measurement of rectal temperature, pulse rate and sweat production is relatively easy, but accurate determination of skin temperatures requires the use of radiometers. These instruments are difficult to use as

require constant, careful calibration. Because of this, skin temperatures are also often discarded. This omission leaves sweat loss, rectal temperature and pulse rate as the chief criteria. The response of the sweat rate to any given change in conditions is by far the greatest. Therefore, this is probably the most sensitive and accurate of these determinations.

Having thus established physiological criteria for evaluation of imposed heat load, it is important to consider the equipment and subjects. The success or failure of such experiments will depend largely upon the chamber used and the subjects selected. Rigid control of ambient conditions within the experimental chamber is essential. Since the over-all heat loss from the body is determined by the combination of wet and dry bulb temperature, radiation, and air movement, it is quite apparent that all of these factors must be very carefully controlled. Small variations in wet or dry bulb temperature, wall temperature or wind velocity under severe environmental conditions will oftentimes produce more marked physiological changes than the garments themselves. The chamber should be such that it will maintain wet and dry bulb temperatures within $\pm 1.0^{\circ}$ F. It is essential that this control be maintained throughout the daily experimental period as well as from day to day. Wall temperatures, including ceiling and floor, must be similarly controllable so that the radiation factor is constant. Wind velocity should not vary more than ± 0.1 mile per hour. The miscellaneous equipment required includes a treadmill, providing very constant and reproducible walking speeds, a balance of sufficient sensitivity to weigh the subjects to within ± 5 grams, rectal thermometers and cardi tachometer or stethoscope. The cardi tachometer is preferable for recording pulse rate since it supplies a permanent record and is not subject to the errors of personal interpretation. With this equipment, there has been constituted a rigidly controlled environment in which work of a prescribed, reproducible rate may be performed which is equipped with instruments enabling the measurement of the expected physiological changes.

What of the experimental subjects? As far as can be determined, men of any bodily size or configuration are suitable. However, it has been generally found that individuals of the pyknic type are rather unsatisfactory in that high temperature exposures are more difficult for them and their results are not as reproducible as others. Under any circumstances those selected should be physically vigorous and willing to undergo arduous exposures to high temperatures over extended periods of time. It is also essential that they realize that fairly regular eating and sleeping habits must be maintained and that excessive indulgence in alcohol be strictly avoided throughout the period of the test. After their selection, all subjects must be physically trained and acclimatized. Both training and acclimatization affect the subjects' physiological responses to any given set of conditions. A trained man completes a prescribed period of walking

on the treadmill with lower pulse rate, rectal temperature, skin temperature, and less weight loss. The same is true in the case of acclimatization. Obviously, therefore, untrained and unacclimatized subjects would not in a basal state and could not be expected to achieve reliable or reproducible values from day to day until they had been so conditioned. The results would be worthless. Training and acclimatization should be carried out under conditions which duplicate those outlined for the test routine. Both can be accomplished simultaneously. Five days of exposure to the exercise and ambient conditions to be used in the test procedure will suffice. The major portion of acclimatization is known to be completed within this period of time and, if the subjects are in reasonably good condition initially, no further training will be required.

Before setting up the exact routine to be used in evaluating the garments, it is essential that the criteria for differentiating them be established. The physiological data, as outlined, will include pulse rate, rectal temperature, sweat loss, and possibly skin temperature. In the first place must be realized that there is no absolute standard with which these values may be correlated. The physiological responses of different individuals to the same heat stress are extremely variable and pulse, sweat rate and rectal temperature bear no simple relationship to the working ability or the likelihood of failure in an individual. Therefore, all evaluations must necessarily be comparative, i.e., responses of the same subject must be compared. It would be extremely difficult to perform a physiological experiment of the type required with a sufficient number of subjects to rule out inter-individual differences. The performance of a subject in one garment must be compared with his performance in another. This can be done accurately as long as experimental conditions are as carefully controlled as outlined. What, however, should be used as the ultimate standard of comparison? Some of the criteria which might be considered are as follows: (a) the absolute limits of temperature and humidity the subject can stand while wearing the test uniforms, (b) the extent of the physiological changes induced by standard work periods in the garments being studied, or (c) the amount of work required to induce specified physiological responses in subjects wearing these uniforms. Any one of the methods may be used. In some instances a knowledge of the upper limit of temperature or work which can be tolerated by a group in a uniform will be of value. However, the comparison of the physiological changes induced by standard work periods is the easiest and simplest approach. Naturally a standard garment will have to be selected as the basis of comparison. If a new uniform is being considered, the one it is intended to replace may be used as a standard of comparison.

Comparative experiments of this type require special consideration in order to insure proper control. In addition no conclusions should be drawn unless they can be supported by statistical analysis of the data. Certain

arbitrary limits over and above statistical significance may be established. Either type of consideration requires that the reactions of individuals be compared only among themselves, *i.e.*, that there be no inter-individual comparisons. This means that all subjects in a test group must wear all of the test items. Thereby an individual's reaction in one outfit can be compared with that in another outfit. Likewise, it is essential that experimental items be rotated among subjects according to a Latin Square technique and that, in any single phase of the work, all items undergoing comparison be represented. If only two subjects can walk on the treadmill simultaneously, only two uniforms can be compared. On the first experimental day each subject wears one of the two uniforms; on the second day the types are exchanged. Thus a maximum of control is obtained. For adequate statistical consideration of such paired data a sampling of at least six and preferably eight or ten subjects is required. In accordance with the material outlined above the data considered will include weight loss during the period of exercise, the rectal temperature, pulse rate and skin temperature at the completion of the period of exercise.

Thus far nothing has been said concerning such details as length of exercise period, severity of exercise and ambient conditions to be used. No categorical statements can be made. Some investigators have employed 4-hour periods, thus insuring that equilibrium between heat production and loss will have been attained. Others have used only 1-hour periods, since differences in garments will have appeared by this time even though equilibrium may not have been reached in some instances. Experience at the Climatic Research Laboratory has shown this to be a suitable method. Under any circumstances all experimental subjects should undergo a definite pre-exercise rest period in the chamber. Only by this means can a fairly standard state in all subjects be assured for the beginning of the testing period. The severity of the exercise may vary considerably. However, an attempt should be made to duplicate the field conditions expected. Great care must be taken to adjust the exercise to the ambient conditions in order to avoid imposition of too great a burden upon the subjects. The ambient conditions under which testing has been carried out have varied considerably. Obviously it is desirable that the garments be investigated under conditions of temperature, humidity, radiation and air movement similar to those under which they are to be used. Significant differences are more likely to be revealed when certain ambient conditions are used. However, if the garment is never used under such circumstances the difference is meaningless.

Strictly speaking, the subjective appraisal of test items has no place in a discussion of techniques of evaluating heat load. However, there are certain features of garments which are exposed remarkably clearly by wear under simulated tropical or desert conditions, namely, drag (the tendency of garments to restrict motion by adhering to the skin), skin

sensation and subjective coolness. They are equally as important. The imposed heat load in determining whether or not a uniform will be accepted. Because of this it is probably desirable, in all garment comparisons, to obtain an interview at the completion of the comparison in which all subjects are asked to rate the garments in the order of their preference in regard to (1) coolness, (2) drag, (3) skin sensation, and (4) overall preference. The data obtained may be analyzed statistically.

Through correlation of physiological and subjective data, collected as outlined above, one may form a reasonable conclusion as to the overall acceptability of any uniform for wear under tropical or desert conditions.

11. WEAR TESTS

E. Folger Taylor

A specially designed garment, or a garment of standard design made of special fabrics or treated fabrics, must be proved for wearing ability before it can be adopted for general use by the Army. Wear tests of several types are commonly used. Accelerated wear tests, in which the garments are continuously subjected to severe wear conditions simulating those countered in combat, are used to evaluate the performance of the garments in terms of a standard garment. Normal wear tests, during which the garments are worn in the usual routine of training, maneuver, and garrison work, compare the performance with that of the standard garment under the same conditions. Special wear tests, in which a group of subjects wear the garments under carefully controlled conditions, evaluate a particular property of the garment. Such tests may take advantage of natural or artificial environments depending on what property of the garment is being studied.

Accelerated wear tests are made by the Quartermaster Board at Camp Lee, Virginia, on a combat course designed to expedite tests of clothing design, construction and materials under simulated rigorous field conditions.

The combat course is illustrated in Figures 11 through 16 and consists of 22 obstacles, each representing a definite tactical problem and apparatus that might be encountered in most theaters of operation.⁸⁰ The course is 1700 feet long and each obstacle was selected after an exhaustive search had been made of clothing failures in the field. Thousands of garments that had been salvaged in the theater of operations and the continental United States were carefully analyzed; combat motion pictures were studied; enlisted and commissioned personnel just returned from combat areas were questioned; and expert clothing technicians were consulted. As a result the simulated tactical problem which was set up was the

⁸⁰ Figures and details of description furnished by the Quartermaster Board, Camp Lee, Va.

troops approaching and attacking an enemy village and then continuing on to wipe out an enemy strong point.

The test subjects traverse the course by rushing, crawling, creeping, climbing, sliding and jumping. From their first vantage point at the start of the course the soldiers run and take cover behind several natural objects as they approach a railroad embankment, where they climb a retvetment, squirm across the heavy coarse slag of the railbed on their stomachs and slide head first down a 30° slide of Belgian Block about 20 feet long. At the bottom they scramble to their feet, run and drop behind a split rail fence. Then the fence is climbed quickly and the soldiers run



Courtesy of Quartermaster Board, Camp Lee, Virginia.

Figure 11 Wear test combat course: Descending 20-foot Belgian Block slide

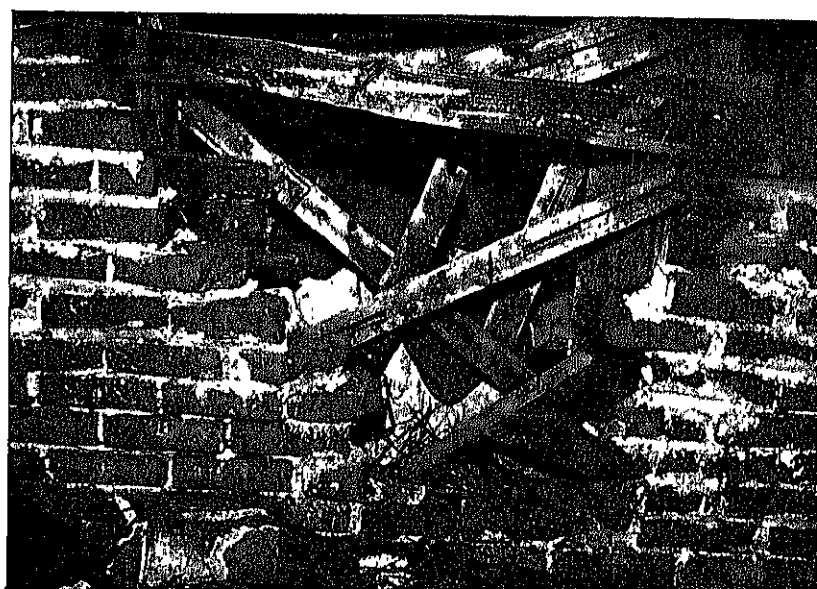
to take cover behind a stone wall. After crossing the wall they run forward taking momentary cover behind trees and logs until a slit trench is reached. Here the test subjects rest and then climb over a tree block and advance to a crushed stone road which must be traversed on the stomach. A series of trenches, a road block and finally a cement culvert are traversed before the enemy village is reached.

The village consists of three bombed out houses. The soldiers enter through the window of the first house, make their way under fallen beams, over passages strewn with cement and rubble, up and down wrecked stairways. They traverse two such dwellings in succession and finally cross from the second dwelling to a ruined warehouse by means of a fallen beam. Here the test subjects are confronted by a maze of narrow twisting



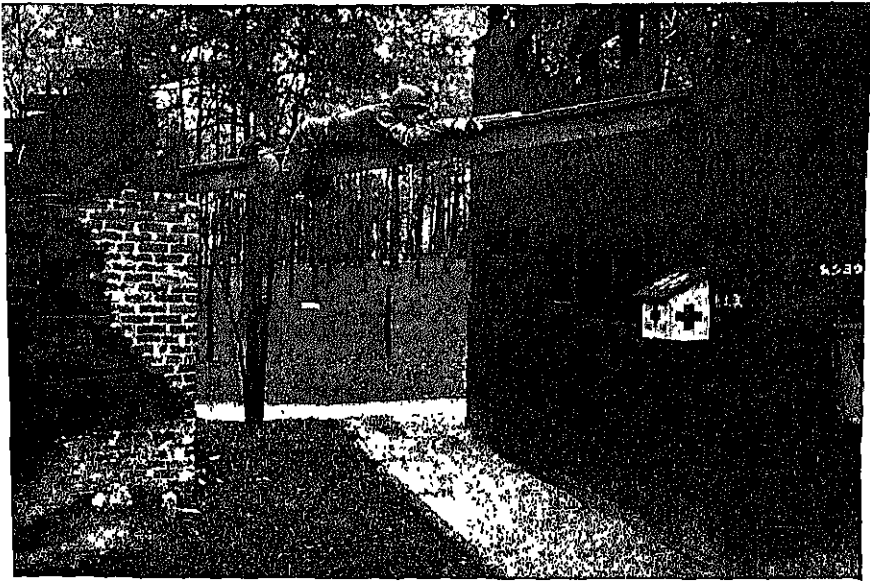
Courtesy of Quartermaster Board, Camp Lee, Virginia

Figure 12. Wear test combat course; Crossing stream on fallen timber.



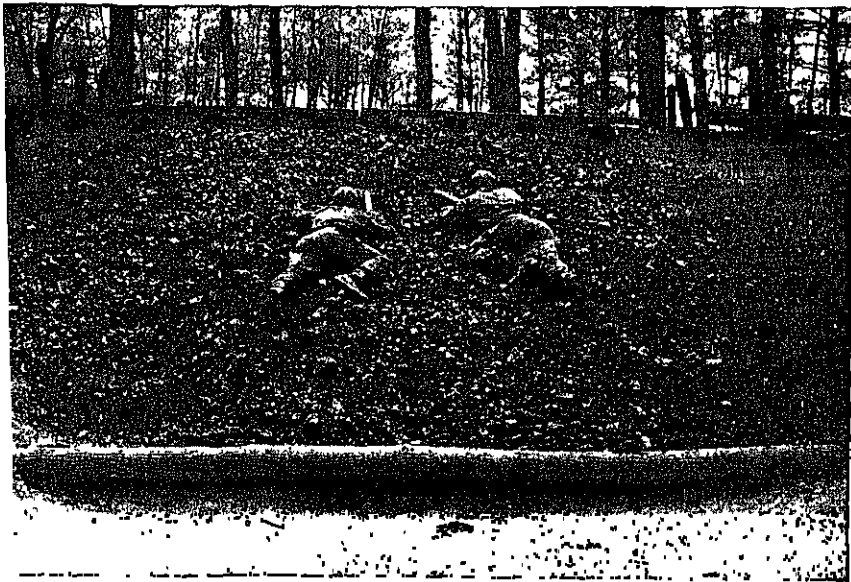
Courtesy of Quartermaster Board, Camp Lee, Virginia

Figure 13. Wear test combat course; Crawling through rubble of bombed-out house.



Courtesy of Quartermaster Board, Camp Lee, Virginia.

Figure 14. Wear test combat course: Crossing from ruined house to warehouse on fallen beam.



Courtesy of Quartermaster Board, Camp Lee, Virginia.

Figure 15. Wear test combat course: Climbing slag railroad embankment.

passageways between jumbled packing cases and, as the soldiers work the way through them, every inch of clothing is subjected to strain and abrasive action. Following the village is another railroad embankment which must be climbed and crossed by crawling, after which the soldiers creep and crawl through a logged communication trench and network of forward trenches. As the final objective, the enemy strong point is approached, the soldiers squirm on their backs under a wire entanglement roll over a road block and slide down a cement lined tank trap, completing the traversal of the combat course.

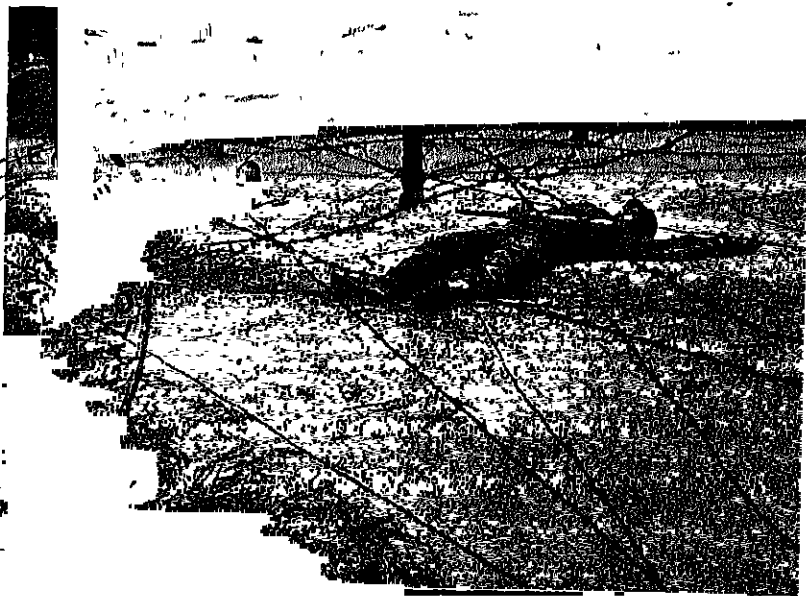


Figure 16. Wear test combat course: Squirming under wire entanglement.

To evaluate clothing by means of this course a group of men outfitted with properly fitting garments are sent over the course as many times as are needed to make the garment unserviceable. The use of correctly fitted garments is of the utmost importance if valid test results and conclusions are to be obtained. After each traverse of the course, the nature, location and extent of deterioration or failure are observed. Traverses of the course are made by the group using control garments as well as the experimental garments and an analysis and comparison is made of the extent and rate of deterioration and failures. Since it is possible for a man to traverse the course several times a day and since the best garments rarely stand many as twenty-five traverses before becoming unserviceable, this course will yield, in a matter of days, information which would take months to obtain from field tests.

Normal wear tests consist of a systematic observation of the manner in which various garments perform under whatever conditions of practical use are desired. For instance, a group of subjects may be equipped with test and control garments and permitted to go about their normal duties. Weekly observation of how the garments are wearing can then be made either before or after laundering, or both, throughout the life of the garment. For the best comparison, it is preferable to select groups of test subjects whose normal duties are the same so that the wear may be related, if possible, to the duty. In this way performance of the new garments under conditions of garrison duty, training, maneuvers, can be studied and correlated with the performance of the standard items.

Details of such tests depend upon what performance characteristics the observers wish to study. For instance, in one wear test of flameproofed clothing the object was to determine the wear life of the garment and the flameproof finish when the garments were worn eight hours a day, doing routine duties at an Army laboratory. The garments were laundered once a week using the Army mobile laundry equipment and the standard washing procedure. Each week garments were dropped from the test at random and specimens were selected from worn portions of the garments as indicated in Figure 17. Some of these specimens were taken before laundering, the remnants of the garments were then laundered and a second set of specimens taken.

These specimens were tested for tensile strength by the raveled strip method as a means of determining the deterioration of the fabric and for flameproofing by both the 45°-Microburner and the Vertical-Bunsen burner tests to ascertain the extent to which the flameproof finish had failed. The selection of specimens before and after laundering permits a differentiation of the deterioration caused by wear and that caused by laundering. In addition to the deterioration of objective qualities such as tensile strength and flame resistance, a subjective evaluation of the garments can be made on the basis of comments that test subjects have to make about the garments. Tests as outlined above should, of course, be conducted to give data which can be evaluated statistically so that confidence may be placed on the validity of the test results.

Special wear tests can also be designed to evaluate some particular aspect of clothing, or clothing treatments. In the case of flameproof clothing, for military use, it is important to evaluate the action of sweat, rain and sea water on various flameproof finishes. The effect of sweat on the flameproof garments can readily be evaluated in conjunction with the physiological heat load tests. Ordinarily, test subjects do work on a treadmill at a standard rate under conditions of high temperature and high humidity as indicated in the preceding section. The total time of exposure is predetermined and is generally accomplished as the result of a series of work periods. The amount of sweat absorbed by the garments is measured

by weighing before and after use. The action of sweat on the tensile strength and flameproofing is measured on appropriate specimens. Since the action of sweat may be spotty because of the manner in which garments come in contact with the body, specimens should be chosen from various parts of the garment to detect such a difference if it occurs. Figure

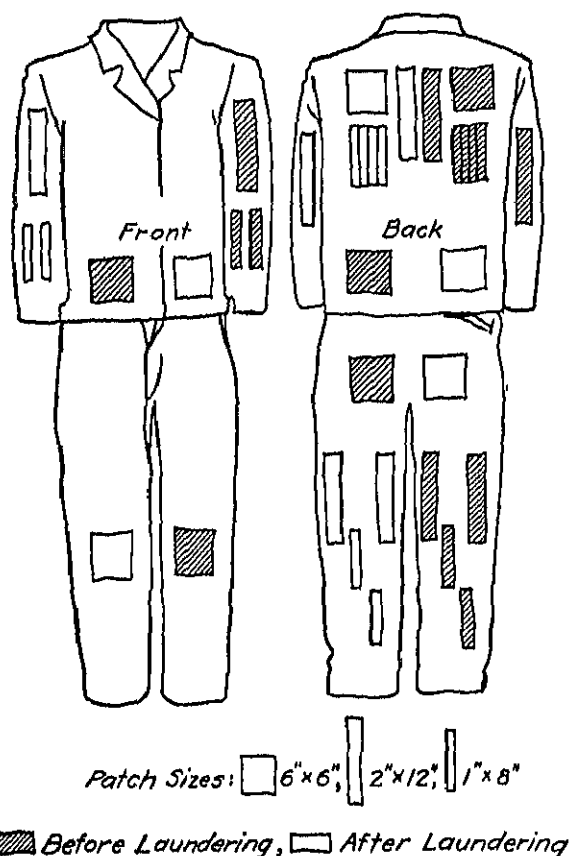


Figure 17. Sampling of worn garments for flame test and tensile test specimens.

17 also represents a suitable method of selecting specimens for this purpose.

The effect of rain is conveniently studied in a so-called "rain court." The rain court is a large room or outdoor space which is equipped with a shower system so designed that the falling water approaches natural rain in drop size and terminal velocity. The rainfall can be adjusted from 0.1 to 3 inches per hour and by operation of auxiliary fan equipment, wind can be superimposed on the rainfall to give the driving effects of a severe storm. In order to maintain the comfort of the test subjects during the

exposure, the test garments are worn over other clothing consisting of underwear, socks, shoe pacs, wet-weather parkas and trousers. Periods of exposure can be set for the convenience of the test subjects and continued exposure can be adjusted to whatever total time is desired or samples can be withdrawn at periodic intervals and tested for tensile strength and flame resistance. In general the type and amount of rainfall exposure to be given a treatment can be decided on the basis of preliminary leaching tests. Easily leachable finishes will need only mild rain treatment for evaluation. Thus in the case of a water-soluble salt type treatment where the objective is to determine the minimum amount of rainfall which will remove the flameproof protection, light rainfall of about 0.1 inch per hour and short exposures must be used. But where a finish does not deteriorate under leaching it is sufficient to show that a specific number of hours of heavy rain, *e.g.*, 3 inches per hour, do not affect the garment or flameproof treatment.

Sea water immersion tests are necessary because it has been found that durable treatments of the urea-phosphate type and possibly other new types which may be developed from time to time are reduced in flameproofing efficiency after prolonged contact with water containing appreciable amounts of calcium and magnesium ions. Sea water immersions are designed to simulate operational landings. Where troops are disembarked from landing craft on to the beaches in sea water which varies in depth, some or all portions of the body may be wet for various periods of time. While landing maneuvers could be used for such a test, superior information can be obtained by a controlled immersion test in which the landing operation is simulated in reverse. An appropriate beach is selected where the test subjects wade in water up to the knees for a period of time, then up to the waist for additional time, and finally up to the neck. Samples of these garments are selected for tensile strength and flameproof evaluation in such a manner as to differentiate between the different times of exposure to the action of sea water. Details of the test can be arranged to test any effect or series of effects of sea water immersion, as for instance the effect of a series of alternate immersions and launderings.

Wherever susceptibility to detrimental ion-exchange reactions has been noted it may be found expedient to revalue the rainfall tests. It has been shown that unless soft, deionized, or distilled water is used, the results of simulated rainfall tests will be affected by the calcium and magnesium ions customarily found in hard waters.

12. TOXICITY TESTS

John W. Meigs

Toxicity tests of flameproof fabrics include evaluation of toxicity of the basic chemicals used, of the fabric at various stages of manufacture,

storage or shipment, and of the finished fabric as it will be used in the field.

Toxicity of basic chemicals must be considered because certain ones are highly poisonous even in small doses; repeated doses may cause cumulative poisonous effects, or, in the case of flameproof fabrics, basic chemicals might release poisonous substances under certain conditions of high temperature.

Toxicity of flameproof fabrics (including toxicity of solvents, dyes and finishes as well as basic chemicals) at various stages of manufacture, storage or shipment might adversely affect either civilian or military personnel in the Army's industrial or military installations.

Toxicity of the finished fabrics is primarily of concern to military personnel in the field.

Tests for determining toxicity of flameproof fabrics must be chosen according to the particular phase of toxicity in question.

Basic Chemicals. Most of these are well known, as for instance borax, or ammonium phosphates. Experimental data on effects of ingestion, absorption by skin contact or inhalation of fumes are available in the medical literature. In the case of untried chemicals, animal studies must be carried out to determine the minimum lethal dose by mouth, subcutaneous injection, skin application or inhalation in the event that gases or fumes are given off under conditions of high temperature. Life span tests upon small animals, such as rats, may be necessary to determine whether chronic toxic effects may result. Fortunately, throughout the war it was not necessary for the Army to undertake any long-range research on toxicity of basic chemicals in flameproof fabrics.

Manufacturing Processes. Toxicity tests are necessary at times to determine the probable hazards to workers in industry. The hazards usually encountered are inhalation of toxic fumes from open containers of chemicals or skin contact with the flameproofing agent as a result of spills or splashes. In addition, there is the hazard of contact between the finished flameproof equipment or material and the skin of personnel engaged in its manufacture or handling. Toxicity tests to determine the hazards from fumes would have to be carried out upon animals unless data were already available. Spills or splashes are hazardous more often because of the solvent involved than because of the flameproofing agent. However, this hazard could be estimated from knowledge of the toxicity of the various basic ingredients. Finally there is the possibility that a worker may become sensitive to the materials contained in the flameproofing substance. This would become apparent if any worker developed dermatitis and the causal relationship between the flameproofing agent and the dermatitis could be proved by *diagnostic patch tests*. These tests, which should be carried out by the plant physician or other qualified medical officer, would prove only that the particular individual was sensitive to

the material in question and would not give any indication of the number of cases of dermatitis to be expected from use of the material over a long period of time. The technique of this test is similar to that described for the prophetic patch test.

Finished Fabric. The most important toxicity tests, however, from the military point of view are those used to determine whether a flame-proof fabric is suitable for use by military personnel in the field.

If toxicity tests of basic chemicals have not been accomplished, the flameproofing agent or flameproofed fabric is disapproved. However, if there is reasonable evidence that the fundamental chemicals are not seriously toxic, tests are undertaken to discover whether the finished material will cause skin irritation to personnel using it under standard field conditions.

Prophetic Patch Test. The likelihood of development of skin irritation is commonly determined by the *prophetic patch test*, devised by Dr. Louis Schwartz and Dr. Samuel Peck, of the United States Public Health Service.⁴⁰ This method has been extremely useful throughout the war period in toxicological evaluation of fabrics of various kinds, including flameproof fabrics. A rather simplified description can be given as follows: The tests require about 200 subjects representing an average cross-section of the population; that is to say, no attempt is made to screen out persons who give a history of skin sensitivity to various substances unless such individuals are present in a percentage much greater than that which would be found in the population at large. Each material to be tested is cut into squares exactly 1 inch on a side. Areas on the back and arms of test subjects are designated as A, B, C, etc., up to the required number, and the materials are also listed as A, B, C, etc. Each patch is placed on the back or the arm in the designated area and is held firmly in place with a 3-inch square of adhesive with a 1.5-inch square of cellophane in the center to prevent direct contact between the patch and the adhesive tape. This assures that there will be a clear area of skin around the patch and that any reaction to adhesive tape will not interfere with reading of the test. After the patch has been left in place for 48 hours, it is removed, and the reaction is read 15 minutes after the adhesive tape has been taken off. Each preliminary reading is recorded, and 48 hours later a second reading is taken. The reason for the second reading is that redness caused by pressure from the patch or irritation from scratching may interfere with the proper reading of the results. After 48 hours these reactions will have disappeared, and any evidence of skin irritation remaining in the area with which the patch had contact will indicate definite irritation as a result of the patch itself. The subjects are then instructed to return after 6 to 10 days, and at that time patches duplicating the original set are placed in

⁴⁰ Schwartz, L., and Peck, S. M., Reprint 2252, *Pub. Health Reports*, 59, No. 17, 546-557 (1944).

approximately the same positions as before. These tests are read exactly the same way as the first series.

The first series of tests indicates the presence or absence in the original patch of a primary skin irritant (a substance which will produce skin irritation in practically anybody, the first time it is applied to the skin for a short period). Strong acids or alkalis are typical examples of primary irritants. Almost any chemical in a high enough concentration will act as a primary irritant. The second series of tests indicates the number of individuals who have been sensitized to the particular chemical in the first test. For example, the chemicals in patch A may produce no skin action the first time; however, during the 48 hours in which the patch is in contact with the skin they initiate chemical or physiological changes within the skin, so that when it is applied the second time 6 to 10 days later definite skin irritation results. Chemicals are extremely variable in their ability to cause such sensitization; for example, almost everyone can become sensitized quite easily to the irritant in poison ivy; however, extremely few people become sensitized to neoprene rubber or cellophane. Some chemicals are so simple or their characteristics are such that it is impossible for them to cause sensitization.

In the interpretation of the results of these patch tests, great importance is attached to the proposed end use of the particular product. For example, if a flameproof fabric is to be used in tents, it is obviously of little consequence whether it produces a small amount of irritation in human subjects when applied closely to their skin for 2 days. Such a contingency is unlikely to arise under field conditions. It is therefore possible to approve for tentage a relatively irritating flameproof fabric. On the other hand, if it is desired to use a flameproof fabric in clothing, much more rigid standards apply. If it is anticipated that the clothing will come in intimate contact with the skin of the neck or the body, it is desirable to select a material which gives no more than one reaction, and preferably a mild one, in 200 subjects. This may not always be possible because such clothing must be used in certain situations regardless of whether it is somewhat irritating to the skin. It is obviously better to have a soldier with an irritated skin than one who has been badly burned. These decisions on toxicity require maximum cooperation between the technical personnel concerned with development of the project and the medical authority making the decision. The latter must present the situation to the agency requesting the test, point out the desirability of using non-irritating chemicals and indicate which of the available samples of flameproof fabrics tested are the least irritating.

The greatest single problem in carrying out prophetic patch tests has been that of obtaining an adequate number of test subjects and retaining them for the 2 series required. Because the tests involve a certain amount of inconvenience, many subjects fail to return for the second series. Sin

the latter determines the probability of sensitization by the material in question, it is even more important than the first series. It is therefore highly desirable if results are to have optimum statistical significance to keep 200 volunteers throughout the test. Unfortunately this goal has only rarely been achieved, and results, although sufficient for a conclusion, have often not permitted unqualified approval of materials. It is believed that agencies requiring evaluation of materials by a patch test should consider supplying volunteers, since such agencies are often in a better position to arouse enthusiasm for the project than any other organization.

Field Test. An additional procedure for testing the finished fabric is the field test. This has not been used very widely to evaluate possible toxicity of flameproof fabrics. During wartime the method was limited in its usefulness because it was too time-consuming and the required professional and technical personnel were not available to carry out tests and record results in the detailed manner necessary for sound scientific conclusions. At present with neither time nor personnel at a premium this method, realistically carried out, should be used to augment the prophetic patch test and other means of evaluating toxicity of flameproof fabrics. Well-conducted tests with records kept by observers trained to recognize toxic skin reactions would go far to establish a better correlation between the results of patch tests of fabrics and the effect of their actual use.

In summary, toxicity tests of flameproof fabrics require consideration of basic chemicals, manufacturing processes and finished fabrics. Since data have usually been available about basic chemicals and manufacturing processes, the greatest amount of new work has been done in testing toxicity of finished fabrics. The possible skin-irritating properties of such fabrics have been of chief concern to the Army, and these have been evaluated in many cases by using the prophetic patch test. In the future, evaluation of toxicity of flameproof fabrics by accurate field test should supplement other methods.

13. RELATED TESTS

R. D. Wells

a. Water Repellency

Though the term "water repellency" is often misused, in the technical sense it relates solely to the hydrophobic nature of a material or surface as distinct from the more general property of "water resistance." The latter is a total effect dependent on both the repellent or non-wetting nature of the material and the impedance or blocking of flow of water by the material mass itself. The relationship of the several contributing factors involved in the complex system of fibers and yarns of a textile fabric is beyond the scope of this chapter. However, the common tests for water-

resistant fabrics are divided into simple categories in accordance with the two major factors mentioned above though the distinction may not be of an absolute nature.

Of the repellency tests, the "spray" test^{41,42} has had the longest use and still serves a useful control function in the finishing of any material. A rating of repellency is assigned according to the amount of water observed to adhere to the fabric after a certain quantity of water is sprayed on it under standard conditions. The sample is mounted flat against a six-inch hoop and clamped on by a slightly larger hoop, then mounted at a 45° angle to the horizontal with its center six inches under the spray nozzle. The standard nozzle contains twenty holes 0.035 inch in diameter, connected to a conical funnel. For the test, 250 ml. of water is poured quickly into the funnel and allowed to spray on the sample. The surface water droplets are then shaken off by tapping the sample, and the amount of water adhering to the sample is compared visually with a graduated series of standard pictures and assigned a rating of 0, 50, 60, 80, 90, or 100 according to the designated rating of the picture most nearly matching the appearance of the sample. The 100 rating is the highest, indicating no visible adhesion of water. A modification of this method in which the adhering water is weighed is included in A.S.T.M. standard D 583-40T.

The dynamic absorption test⁴⁴ has become recognized as a better evaluation of hydrophobic finishes than the spray test. A set of five weighing bottles, each containing 8 by 8 inch samples is placed in 2 liters of water in a 6-liter hexagonal tumble jar, which is then rotated about a transverse axis at 55 R.P.M. At the end of a designated time interval the samples are removed and weighed individually through a standard wringer, once alone and once between dry blotters. The water absorption is then determined by weighing the wet samples and comparing with the dry weight. This test may be modified to attain an absorption rate by removing the samples at stated intervals until equilibrium is attained. It has an advantage in that it may be used for comparative purposes where the fabric samples are not of identical physical construction, though some reservations should be made when widely different fabrics are compared. It is a measure of the efficiency with which the finish reduces the natural absorbency of the fabric, and is dependent both on the inherent properties of the finishing compound and on the degree and uniformity of the application. It has further validity as a test of the degree of uniformity of the application.

⁴¹ Textiles; General Specifications, Test Methods—Fed. Std. Stock Catalog, Series III, par. 5a(1)—CCC-T-191a.

⁴² A.A.T.C.C. Tentative Method—Standard A.A.T.C.C. Test Methods, 1943 Yearbook, p. 236.

⁴³ A.S.T.M. Designation: D 583-40T; A.S.T.M. Standards on Textile Materials (1944), p. 106.

⁴⁴ Textiles; General Specifications, Test Methods—Fed. Std. Stock Catalog, Series III, Par. 5b(1)—CCC-T-191a.

test of value of the finish in that the motion of the sample in the immersion bath breaks down the false resistance to initial wetting caused by entrapped air, which in some other tests gives misleading evaluations.

The water-resistance tests in which the total effect of fabric and finish is measured are of two general types: hydrostatic pressure and simulated rainfall. Federal Specifications⁴⁵ and A.A.T.C.C.⁴⁶ and A.S.T.M.⁴⁷ standards outline the conventional hydrostatic pressure test in which the height of the steadily increasing column of water imposed on the sample is recorded when the water penetrates the fabric. The sample is clamped over a standard orifice, and the hydrostatic load applied by raising a connected reservoir with mechanical drive, or by a constant feed device, so that the level is increased at a rate of 1 cm. per second. The height of the column is then recorded at the time that the third drop of water appears at different places through the sample. This type of test has been widely used for many years though its applicability for many materials, particularly clothing fabrics, is subject to question. A percolation test⁴⁸ uses a similar apparatus except that the hydrostatic head is maintained at a designated level and the amount of leakage measured. Both tests are sensitive to the manner in which the hydrostatic load is applied, and to changes occurring within the fabric as the fibers swell in wetting out. For coated fabrics and other supposedly continuous films, however, those limitations do not apply. Such tests may also be the best adapted for evaluating the fabric without regard to hydrophobic finish provided that the hydrophobic forces are overcome either by a shock load or protracted time.

For clothing fabrics in particular the simulated rainfall tests are finding increasing favor. With the exception of the apparatus described in the Federal Specification,⁴⁹ and the Bundesmann apparatus used in European laboratories, the various rainfall devices have not reached a state of official standardization. As would be expected, however, being nearer to the natural conditions of usage, correlation with service tests has been more nearly approached. The main limitations to date are in providing the same dynamic forces in the drop impact as occur in nature without going to the approximately 20-foot free fall required to reach terminal velocity, and in presenting the sample to the shower in a realistic fashion as to shape, backing, and motion. It has been possible for the Army to

⁴⁵ Textiles; General Specifications, Test Methods—Fed. St'd Stock Catalog, Sect. IV, Par. 5c(1)—CCC-T-191a.

⁴⁶ A.A.T.C.C. Tentative Method—Standard A.A.T.C.C. Test Methods, 1943 Year-book, p. 232.

⁴⁷ A.S.T.M. Designation: D 583-40T; A.S.T.M. Standards on Textile Materials (1944), p. 104.

⁴⁸ Textiles; General Specifications, Test Methods—Fed. St'd. Stock Catalog, Sect. III, Par. 5c(2)—CCC-T-191a.

⁴⁹ Textiles; General Specifications, Test Methods—Fed. St'd. Stock Catalog, Sect. III, Par. 5c—CCC-T-191a.

make use of full-scale rain rooms and outdoor rain courts, with water drop size and distribution equivalent to natural rainfall in three ranges of intensity from 0.1 inch per hour to 3 inches per hour. In such tests for garment fabrics, the garments are worn by human subjects traversing the rain area. However, these facilities are not readily available to most agencies, and dependence must be placed on one or more of the more convenient procedures. The selection of the most applicable test method should always be based on the following considerations: (a) the conditions of use or service for the material in question, and (b) the importance of the finish, fabric, or total performance in the evaluation being made.

b. Mildew Resistance

Many types of tests for mildew resistance have been proposed and practiced by research and procuring agencies. The differences are due in part to the facilities available within each agency and the scientific background of the personnel responsible, and in part to the type and expected use of the materials in which the individual agencies are most interested. The resulting confusion in evaluation standards has drawn the attention of not only the procuring services but also the National Bureau of Standards, Federal Specification Board, National Defense Research Committee, American Society for Testing Materials, and the American Association of Textile Chemists and Colorists, all of whom have taken an active part in the effort to resolve these different tests and establish generally recognized procedures. As of this date, however, the effort has met only partial success, largely because of the difficulty in correlating any accelerated tests with the complex phenomena encountered in natural exposures.

A distinction is generally recognized, though admittedly vague, between "mildewing" and "rotting"; the former describing a visible growth of fungus on the material in which tendering may or may not result, and the latter indicating microbiological attack on the material without regard to the extent of visible "mildew." In a relatively small class of material such as camouflage garnishings, "mildew" as described above is the predominating consideration because of the effect on the color of the material. With most materials, however, the prevention of "rotting" is the aim of the fungicidal treatment and the tests are meant to measure the efficiency of this protection even though they are called in common usage "mildew-resistance tests."

Pure Culture Tests. These tests are those in which the sample is inoculated with the spores of a specific fungus organism, placed in a warm incubation chamber under high humidity conditions for a stated length of time, and evaluated either by visual evidence of fungus growth on the sample or the extent of damage in terms of breaking strength. The many variations lie in the choice of test organism from the hundreds which

might be suggested, in the condition of the organism at the time of inoculation (spores only, or spores and flourishing hyphae), the mineral and organic nutrients supplied in the test, and the temperature and moisture conditions. An example of this type, which has probably had the longest and most general usage is the "Chaetomium globosum" test.⁵⁰ (Methods similar to this have been listed as tentative standards by A.S.T.M.⁵¹ and soon will be listed by A.A.T.C.C.) Though in practice a visual examination of the incubated sample has often been used for the sake of convenience, the interpretation is in terms of rot resistance as *Chaetomium globosum* is known to be an active cellulose destroyer. An example where a superficial fungus (not an active cellulose destroyer) is used is the "Aspergillus niger" test for camouflage materials.⁵²

Pure culture tests have the theoretical advantage of reproducibility, but are often criticized as being unrealistic due to the arbitrary choice of organism and conditions. A group of tests using either known or unknown multiple inoculum have been proposed as compromises between more natural conditions and reproducibility. An example of this type, in which part of the inoculum is derived from the soil, is the enriched soil suspension test.⁵³ It has been possible to obtain consistent results with this type of test within an individual laboratory, but correlation between laboratories has not been of a high order.

Soil Burial Test. This test, generally considered the most severe of the accelerated tests, is a direct contrast to the pure culture techniques. Samples are imbedded for a stated length of time in a warm soil rich in humus, and the loss in strength then measured. The inoculum here is a complex mixture of fungi and bacteria in all stages of development together with natural nutrients and probably enzymes produced in the microbiological action on other organic material in the soil bed. Standardization is somewhat difficult because of differences in activity between soils from different sources or within any one soil bed from time to time, and its interpretation is further complicated by chemical or absorptive activity of soil components on fungicides or other finishing agents. The simplicity of procedure, however, recommends it in that it can be conducted without trained scientific personnel; while its severity is such that most materials and treatments which pass it will pass most other accelerated "rotting" tests currently used. On this latter point is based the common criticism that, by reliance on the soil burial test alone, some ma-

⁵⁰ Textiles; General Specifications, Test Methods—Fed. St'd. Stock Catalog, Sect. VIII, Par. 1b—CCC-T-191a.

⁵¹ A.S.T.M Designation D 684-42T; A S T M Standards on Textile Materials (1944), p. 100.

⁵² U. S. Army Specification No. 39-13.

⁵³ Textiles; General Specifications, Test Methods—Fed. St'd. Stock Catalog, Sect. VIII, Par. 3—CCC-T-191a

materials may be excluded which might be reasonably efficient under normal conditions of use. The procedure given in Federal Specification CCC-191a,⁶⁴ is generally recognized, and is in general agreement with that given in A.S.T.M. standards.⁶⁵

As in most technical fields, accelerated tests must be used with discretion. It is common practice to use a variety of mildew-resistance tests in the evaluation of proposed materials or protective finishes, and select those which have given good performance in all tests. It is desirable when possible to conduct actual exposure tests of the material in the most extreme climate (with regard to mildew conditions) and under the most severe conditions of service or storage which the material in question would be expected to undergo. If a certain treatment has been adopted on this basis, it is then customary to check subsequent production of the material by a single test which is selected for convenience and its ability to detect faulty production of the supposedly standardized finish.

⁶⁴Textiles; General Specifications, Test Methods—Fed. St'd. Stock Catalog, Series III, Par. 4—CCC-T-191a.

⁶⁵A.S.T.M. Designation: D 684-42T; A.S.T.M. Standards on Textile Materials (1944), p. 102.

Chapter V

General Flameproofing Processes for the Treatment of Cotton Fabrics

In addition to the evaluation procedures presented in the preceding chapter, those persons who are actively engaged in the development or application of flameproofing processes are, by necessity, also concerned with the nature of contemporary processes and the methods of industrial application. For the benefit of those readers, this chapter has been organized to present the chemical nature of the more common flameproofing processes, a discussion of the mechanisms by which they function, an examination of the laboratory experimentation upon which those mechanisms are based, and, finally, a practical description of the industrial practices employed in their commercial exploitation. Obviously, each different flameproofing process cannot be considered individually. Thus, the available treatments have been grouped according to the general type of flameproofing agent and the method of impregnation, further separating the temporary water-soluble treatments from those of a more durable nature. Since the water-soluble salts have, until recently, predominated the field of flameproofing, it is fitting that this group be considered first.

A. TEMPORARY TREATMENTS

Robert W. Little

1. NATURE OF RETARDANTS

The majority of the interest in flameproofing agents in the past has been concentrated upon the water-soluble retardants. Furthermore, perhaps due to the fact that inflammability is commonly considered a characteristic of organic materials, the investigations have, with few exceptions, been concerned with soluble inorganic salts. The protection afforded by these retardants has been classified as "temporary" since the mildest water leaching or even profuse perspiration in clothing completely destroys the efficacy of the treatment. In some cases the retardancy is seriously impaired by long-term exposure to elevated temperatures or high humidity. For this reason, these "temporary" treatments are ap-

plied with the idea of periodic reprocessing in order to maintain the desired properties of flame and glow resistance. The flameproofing agents to be considered in this section are water-soluble inorganic salts which are generally applied to the fabric by simple immersion in aqueous solution.

In considering the innumerable water-soluble, inorganic compounds which are potential flameproofing agents it should be borne in mind that any material which is flammable will exert an inhibiting action upon the flaming and glowing characteristic of a fabric if added in sufficiently great quantity. The characterization of a substance as a flame or glow retardant should be based upon its efficient performance by way of one of the mechanisms discussed in Chapter III, rather than upon the inhibiting effect caused by the mere dilution of combustible material with large amounts of an incombustible compound or mixture.

A brief examination of the literature on the subject of flameproofing indicates that practically all the common inorganic salts have been investigated as possible flameproofing agents for cellulosic materials. In this attempt will be made here to present or discuss this group of compounds in its entirety. For a comprehensive survey of the salts and mixtures which have been considered, the reader is referred to two of the best bibliographies on the subject of flameproofing.^{1,2} These articles contain nearly 700 references on the subject including over 400 patents. An attempt will be made in the following sections to point out the general types of compounds to be considered and the groups into which they might be classified on the basis of their mode of action.

The efficiency of a compound or mixture as a flameproofing agent will be dependent upon its ability to impart to the fabric a high degree of resistance to both afterflaming and afterglow. As has been pointed out in previous chapters, these two characteristics are quite different and more or less unrelated phenomena which take place by entirely different mechanisms. For this reason many of the better flameproofing agents from the standpoint of prevention of afterflaming fail to impart any appreciable degree of glow resistance to the fabric. Similarly, boric acid, which is one of the better water-soluble glowproofing agents, possesses very little ability to prevent the afterflaming of fabric. Indeed, there are very few available inorganic compounds which are able to produce effective resistance to both afterflaming and afterglow. Outstanding examples of this small group are the ammonium salts of phosphoric acid.

¹ "Fireproofing of Fabrics." Ramsbottom, J. E., and Snoch, A. W., Second Report of the Fabrics Coordinating Research Committee, Dept. of Scientific and Industrial Research (Great Britain), (1930).

² "Bibliography on Flameproofing" Akin, E. W., Spencer, L. H., and Macosko, A. R., *Am. Dyestuff Repr.*, 29, 418, 445 (1940).

a. Flame Retardants

The salts which function in the prevention of afterflaming may be divided into three general groups on the basis of the mechanisms by which they function. These mechanisms have been discussed fully in Chapter III where it was pointed out that some of the accepted theories of flameproofing rest on a more or less sound foundation of experimental data while others are based more on speculation and do not serve to explain adequately the action of flameproofing mixtures. In several cases the physical and chemical properties of the compound make it equally applicable to more than one mode of action. It is highly probable that in the majority of cases a flame retardant is effective due to its functioning by more than one mechanism.

Group I. The retardants in this group consist of salts or mixtures which, when heated, melt at relatively low temperatures and subsequently resolidify in the form of a solid foam produced by the evolution of decomposition products. These materials are effective due to the formation of this foam which is stable to heat and serves as a barrier between the fabric and the flame. The retardants are generally either highly hydrated salts possessing low melting points or mixtures of a low-melting compound with a highly hydrated salt. In some cases the hydrate may be replaced by a carbonate or similar salt which decomposes with the evolution of non-flammable gases. Typical examples of this group of retardants are the following:

Borax $[\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}]$

Aluminum Sulfate $[\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}]$

Borax : Boric Acid (7 : 3) $[\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} : \text{H}_3\text{BO}_3]$

Borax : Boric Acid : Diammonium Phosphate (7 : 3 : 5)

$[\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} \cdot \text{H}_3\text{BO}_3 : (\text{NH}_4)_2\text{HPO}_4]$

Borax : Diammonium Phosphate (1 : 1) $[\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} : (\text{NH}_4)_2\text{HPO}_4]$

Sodium Phosphate : Boric Acid (1 : 1) $[\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O} : \text{H}_3\text{BO}_3]$

Boric Acid : Diammonium Phosphate (1 : 1) $[\text{H}_3\text{BO}_3 : (\text{NH}_4)_2\text{HPO}_4]$

There are many more inorganic compounds and their mixtures which could be included in this group and the efficiencies of the retardants range from the most highly efficient of the water-soluble type to those which can hardly be classed as flame retardants. Of those listed above, the first two compounds, borax and aluminum sulfate, are much less effective than any of the mixtures which follow. Some mixtures which produce voluminous foams, when tested by heating the powdered mixture to 500°C , are found to be non-effective as flame retardants when applied to fabrics. Typical examples would be:

Sodium Carbonate : Boric Acid (1 : 2) $[\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} : \text{H}_3\text{BO}_3]$

Stannic Chloride : Boric Acid (1 : 1) $[\text{SnCl}_4 \cdot 5\text{H}_2\text{O} : \text{H}_3\text{BO}_3]$

In the first case the material remaining on the fabric after impregnation and drying is essentially sodium tetraborate. This is in agreement with the flame test data which indicate this mixture to be approximately equal to borax in its resistance to afterflaming.

In the second case it was found that the foam did not form until the mixture had been heated for some time at 400–500° C. It appeared, therefore, that the fabric had been consumed by flame before foam formation occurred.

The efficiency of a retardant of this group, then, will depend upon the extent to which the mixture satisfies the following requirements:

1. One component, at least, must decompose at a relatively low temperature (80–200° C.) with the evolution of large amounts of gaseous products (H_2O , CO_2 , NH_3 , SO_2 , etc.).

2. The other component must melt at a low temperature near that at which gas evolution begins. The mixture should form a uniform melt which solidifies as decomposition progresses.

3. The foam formed as the evolved gases blow up the solidifying melt must be formed at a low temperature, without long heating and be stable at temperatures as high as 500° C.

These flame retardants of Group I are generally the most efficient of all the water-soluble type in the prevention of afterflaming. At add-ons of only 10 to 12 per cent these mixtures prevent any afterflaming and also reduce greatly the damage which the fabric suffers while in contact with the igniting flame.

Group II. The flame retardants of this second group consist of inorganic acids, acid salts or salts capable of liberating acids on heating. In general these flameproofing agents are less effective than those of Group I in the prevention of afterflaming but have the advantage of being quite effective in the inhibition of afterglow. The following are representative of this type of retardant:

Orthophosphoric Acid $[H_3PO_4]$

Monoammonium Orthophosphate $[NH_4H_2PO_4]$

Diammonium Orthophosphate $[(NH_4)_2HPO_4]$

Monosodium Orthophosphate $[NaH_2PO_4 \cdot H_2O]$

Sulfamic Acid $[NH_2-SO_2-OH]$

Ammonium Sulfamate $[NH_2-SO_2-O-NH_4]$

Ammonium Sulfate $[(NH_4)_2SO_4]$

Ammonium Molybdate $[(NH_4)_2MoO_4]$

Zinc Chloride $[ZnCl_2]$

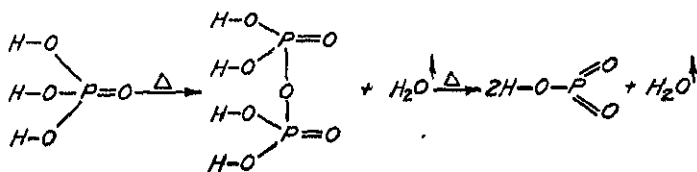
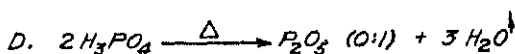
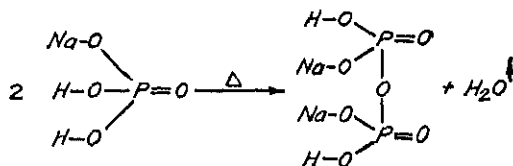
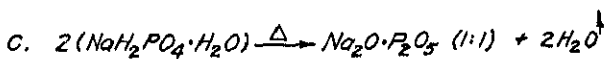
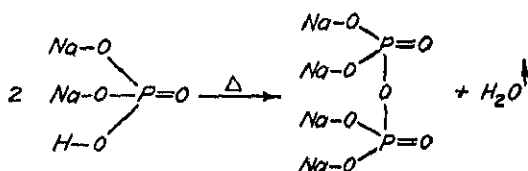
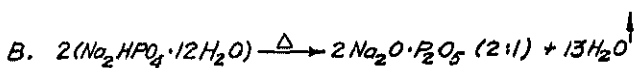
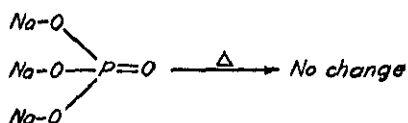
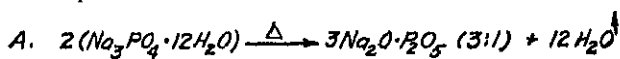
Antimony Oxychloride $[SbOCl]$

Aluminum Sulfate : Monoammonium Phosphate $[Al_2(SO_4)_3 \cdot 18H_2O : NH_4H_2PO_4]$

Ammonium Sulfamate : Diammonium Phosphate $[NH_2-SO_2-O-NH_4 : (NH_4)_2HPO_4]$

The efficiency of these compounds and mixtures in the prevention of afterflaming appears to be dependent upon the ability of the retardant to furnish a free acid group at the time of incipient flaming. The function of

this free acid in the prevention of afterflaming has been previously discussed in Chapter III. That this is the primary requirement of this group of retardants is illustrated by the relative efficiencies of orthophosphoric acid and its sodium salts. When the acid anhydride is balanced by an equivalent amount of alkali oxide in the combustion residue, the salt does not possess flame-retardant properties. Bearing in mind the formation of the pyrophosphate at approximately 200° C., the reactions on heating could be represented as follows:



Equations for chemical reactions; heating of sodium phosphates.

The requirement of the presence of the free acid groups in order to function in the prevention of afterflaming is illustrated by the flame test data presented in Table 1.

Table 1. Relative Flame Retardancy of Orthophosphoric Acid and Its Sodium (45°-Microburnor Flame Test)

Compound	Add-On %	Afterflaming sec.	Char Area in ²
$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	77.5	3	C.C.*
$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	57.4	60	C.C.
$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	16.9	1	2.4
H_3PO_4	14.8	0	2.5

* C.C.—Completely consumed by afterflaming and afterglow.

Trisodium orthophosphate does exhibit a slight flame retardancy it is of low order and probably attributable to another mechanism than that of the compounds of Group I. The disodium salt shows a slightly more efficient action in slowing the burning rate but still could not be classified as an effective flame retardant. The monosodium salt and the acid itself are fairly efficient flame retardants as shown by the results obtained at the relatively low add-ons indicated.

The requirements for the members of this group will be clearer if the reader will refer briefly to the discussion of the dehydration and the mechanism of flame retardancy as discussed in Chapter III.

Group III. The third general group into which the soluble, inorganic flame retardants may be subdivided consists of those compounds which decompose or sublime on heating, evolving large amounts of non-inflammable gases or vapors. The members of this group in general consist of carbonates, chlorides, ammonium salts and highly hydrated salts. As pointed out in the fundamental discussions of Chapter III, this mechanism of flameproofing by the generation of a non-inflammable atmosphere is not as credible nor as well substantiated as the other two and in many of the compounds in this group have been, or might be, assigned to one of the other two groups. The following will serve as examples:

Hydrated Sodium Carbonate $[\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}]$
 Ammonium Chloride $[\text{NH}_4\text{Cl}]$
 Ammonium Bromide $[\text{NH}_4\text{Br}]$
 Ammonium Iodide $[\text{NH}_4\text{I}]$
 Ammonium Sulfate $[(\text{NH}_4)_2\text{SO}_4]$
 Ammonium Sulfamate $[\text{NH}_4\text{O}-\text{SO}_2-\text{NH}_2]$
 Sodium Tungstate $[\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}]$
 Trisodium Orthophosphate $[\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}]$
 Calcium Chloride $[\text{CaCl}_2 \cdot 6\text{H}_2\text{O}]$

There are a few members of this group of compounds which, as cannot readily be assigned to either of the other mechanisms. The outstanding examples are the ammonium halides. They exhibit no foaming tendencies on heating alone and also very little decomposition to the corresponding halogen acids. It may be that they will fall into Group II when more is known about the course of their thermal degradation reactions in the presence of cellulose and its decomposition products. Extensive dis

ciation into ammonia and the halogen acid has been reported in the neighborhood of 350° C. but thus far the flame-retardant properties seem to be related more to the ease of sublimation and the amounts of sublimate formed.

It is possible that in many cases the flame-retardant action of a compound is enhanced by this formation of a non-inflammable atmosphere or dilution of inflammable gaseous products. This would seem, however, to be a secondary rather than a primary cause of flame retardancy.

b. Glow Retardants

The water-soluble compounds which are effective in the prevention or inhibition of afterglow are limited almost entirely to boric and phosphoric acids and their acid salts. As was similarly pointed out in the discussion of flame retardancy, many compounds exhibit anti-glow tendencies but only at excessively high add-ons. This could be attributed to the great amounts of added material merely preventing oxygen from coming in contact with the carbonaceous char. Discussion of the mechanisms of afterglow in an earlier chapter have pointed out that true glow retardants are effective at exceedingly low add-ons and apparently function by catalytically influencing the oxidation of carbon.

The compounds of boric and phosphoric acids are effective in the prevention of afterglow only when the salt will decompose at flame temperatures or below to yield a free acid group. In cases where the acid anhydride is balanced by an equivalent amount of alkali or alkaline earth oxide the salt does not possess glow-resistant properties. A convenient example of this effect is orthophosphoric acid and its sodium salts. The reactions occurring on heating these compounds were discussed in the preceding section under the flame retardants of Group II. Employing similar data for illustrative purposes, the requirement of the free acid groups in order to function in the prevention of afterglow is clearly shown by the following flame test data.

Table 2. Relative Glow Retardancy of Orthophosphoric Acid and Its Sodium Salts (45°-Microburner Flame Test)

Compound	Add-On %	Afterglow sec.	Char Area in ²
$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	77.5	400	C C.*
$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	57.4	70	C C.
$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	16.9	0	2.4
H_3PO_4	14.8	0	2.5

* C C.—Completely consumed by afterflaming and afterglow.

Similar data could be presented for boric acid and its sodium salts in which case borax not only does not exhibit any glow-resistant properties but instead seems to actually enhance the afterglow of untreated fabric.

Of the two principal glow retardants available the acid phosphates somewhat superior to boric acid. In combination with borax in an optimum mixture, boric acid is unable to prevent afterglow. Similar mixtures borax and diammonium phosphate, on the other hand, render the fabric completely glow resistant as well as flame resistant.

2. METHODS OF COMMERCIAL APPLICATION

Water-soluble flameproofing agents may be applied to fabrics by means of several different techniques. In any case the objective is to obtain an add-on which will be sufficient to render the material flame and glow resistant and to distribute the retardant uniformly throughout the fabric. One factor which must be considered regardless of the impregnation technique used is the thermo-labile nature of the majority of flameproofing agents. For this reason care must be taken in drying, mangling or ironing the treated goods. Many of the more common retardant mixtures of the water-soluble type will hydrolyze or decompose at temperatures below those near the standard ironing temperatures of 135-149° C. The mixtures of borax and boric acid lose hydrated water at 127-134° C. and hence prolonged exposure to ironing temperatures will impair the effectiveness of the resultant treatment. Ammonium sulfamate and its mixtures with other compounds decompose in the neighborhood of 134-147° C., depending upon the mixture, and release inorganic acid residues which will reduce the strength of the treated fabric. The ammonium phosphates are not serious offenders with respect to tendering but will lose ammonia, particularly in the presence of large amounts of water, with the resulting formation of acidic residues and tendering of the fabric. In order to avoid undue loss of either flameproofness or fabric strength, the mildest of drying and ironing conditions must be employed. This may be accomplished by allowing the treated fabric to become fairly dry before ironing or mangling. High temperatures may be employed in pressing provided the water can be removed quickly and the fabric does not remain in contact with the iron or mangle long enough to reach the decomposition temperatures. In commercial practice, where dry tumblers are used, the tumblers can be operated at medium temperatures and reduce the risk of loss of strength or retardancy.

The four common methods of applying water-soluble retardants are immersion, spraying, brushing or impregnation in a commercial wash. Because of the great variation in the chemical and physical properties of different flameproofing agents the details of any impregnation technique will vary from one case to another. For this reason no specific method can be outlined which will be applicable to all retardants. An attempt will be made, however, to discuss in the following pages the general methods of treatment. The application of these methods for a specific case will depend

upon the solubility, minimum effective add-on, and similar properties peculiar to the flameproofing agent being considered.

a. Immersion

The dipping of fabrics or garments into a volume of retardant solution followed by hand or roll wringing is the simplest method of application and is adaptable for treating small batches of material in the home. It has one advantage in that it tends to produce a more uniform distribution than can readily be accomplished by means of spraying or brushing. A convenient method of home impregnation is to incorporate the proper amount of flameproofing agent into the final rinse of the laundering procedure. In the case of many of the common commercial preparations this would be approximately one pound of retardant per gallon of water. The final dry add-on required in most cases ranges from 10 to 15%. If the fabrics dipped into the retardant rinse are very wet, the concentration of the solution will have to be greater than given above.

The adaptation of hand dipping to commercial impregnation where large quantities of material are being treated is quite slow and costly. The fabrics should be dried previous to impregnation which introduces an additional drying operation into the usual laundering procedure. In addition, the extra handling increases the labor requirements and considerable retardant is lost in transferring the fabric from tank to extractor.

b. Spraying

In many instances it is advantageous to apply the flameproofing agent to a textile article without removing the article from service. This is particularly true in the case of interior decoration textiles such as drapes, curtains and buntings. The same method is applicable for rugs and slip covers and could be employed for any textile product. The fabric is hung up and sprayed with a highly concentrated retardant solution. Any suitable spraying equipment may be employed provided the spray is not too coarse. The fabric is thoroughly and evenly sprayed until it appears definitely moist. In order to avoid streaking of the fabric on drying the spray should be as fine as possible. With heavier fabrics it is often necessary to apply the spray to both sides of the cloth. This method tends to produce uneven distribution and requires some experience to achieve a satisfactory treatment. In treating curtains and garments in the home a modification of this technique can be used by applying the retardant when sprinkling the fabrics just prior to ironing. The cloth must be thoroughly moistened, however, and as pointed out previously, the fabric should be allowed to become nearly dry before ironing in order to avoid undue decomposition of the flameproofing agent.

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c. Brushing

In the event that a suitable spray gun is not available, a concealing solution of retardant may be brushed onto the fabric. Again, care must be taken to moisten the fabric sufficiently and yet achieve a uniform application in order that the treated material will not have a streaked or mottled appearance.

d. Commercial Laundry Treatment

Where large quantities of clothing or other piece goods are concerned, the only effective and, at the same time, economical method of applying flame-retardant treatments is by mechanical means. The plant best equipped to carry out the impregnation is the commercial laundry since the fabrics generally are laundered prior to treatment, a saving in both time and expense is accomplished by impregnating at the time the fabrics are washed. This type of treatment has been carried out commercially and shown to be practical. The variables which exist and the effects they exert upon the finished garment are presented in the following paragraphs.

In an investigation of the suitability of Army mobile laundry equipment for the application of water-soluble flameproofing agents to herbaceous twill coveralls, the Quartermaster Board at Camp Lee, Virginia, carried out a series of experiments using the standard mobile laundry equipment to apply a water-soluble retardant to combat clothing. The flameproofing agent used was a commercial preparation of the sulfur phosphate type. The equipment and laundering procedures employed were very similar to those used in commercial laundry practice. The washer was a standard 30 by 30 inch wash wheel which rotated at a speed of approximately 30 revolutions per minute and reversed direction every 7 or 8 rotations. The 20-inch centrifugal extractor rotated on a vertical axis at a speed of approximately 1600 revolutions per minute and accommodated about 10 pounds of clothing. The clothes were dried in dry tumblers of the standard open-end type which were 36 inches in diameter and 30 inches long. The laundering procedure employed was the standard mobile laundry procedure which may be briefly described as follows:

Washing.

Load	Type of Solution	Water Level in Washer (in.)	Time per Operation (min)
Approx. 60 lbs. of clothing per run	break suds (1.5 oz. soap)	8	1
	break suds (1.5 oz. soap)	5	1
	rinse	9	1
	rinse	9	1
	rinse (3 oz. sour)	9	1
Total.....			19 1/2

The temperature is maintained between 90° and 100° F.

Extraction. Approximately 70% of the water is removed from the garments by spinning for 5 minutes. One half of the wash load, or approximately 30 pounds, is extracted at one time.

Drying. The extractor load is placed in a dry tumbler for 14 to 20 minutes depending upon climatic conditions and the efficiency of the plant.

Attempts were made to apply the flameproofing agent by including it in the final rinse of the regular laundering process and also by adding an additional rinse after laundering but prior to extraction. This approach led to inconsistencies in the percentage impregnation obtained and in some cases the add-on was below the minimum requirement of $11\% \pm 1$. Consistent add-ons were obtained by applying the retardant in an additional rinse following extraction. Experimentation indicated that with insufficient volume of solution in the washer the garments were not effectively impregnated even after rotation for as long as 15 minutes. A minimum water level of 4 inches was found to be necessary to insure complete penetration of the entire load.

No appreciable saving of the flameproofing mixture was noted in drying the garments prior to treatment. Avoiding this additional drying step was very advantageous since the added process of tumbling the clothing after laundering and prior to immersion in the flame-retardant solution added 20 minutes to the operation. Furthermore, the omission is a distinct advantage in a commercial plant where drying is one of the major problems.

In the extraction process following the flameproofing treatment it is desired to remove the majority of the solution from the fabric leaving a wet pickup of approximately 100%. In the experiments at Camp Lee a constant concentration of solution was used and the wet pickup varied by means of varying the time of spinning in the extractor. It was found that the extraction time was the prime factor in obtaining the desired dry add-on of $11\% \pm 1$. The relationship between extraction time and dry add-on is shown graphically in Figure 1, which indicates that the add-on may range from 17.1 to 3.4% depending upon the duration of the extraction period. In this particular case, using a solution concentration of approximately 10%, an extraction time of 10 seconds was optimum for producing a 100% wet pickup and correspondingly dry add-on of 10%. It is believed that in employing a similar process in a commercial laundry plant it would be preferable to maintain a constant rate of spinning or extraction time and adjust the pickup by variations in solution concentration. This is desirable since a slight variation in concentration in that case would not be nearly as critical as a variation in the extraction time as indicated in Figure 1. It is true that in some instances it may be necessary to vary the extraction time due to the solubility limitations of the particular flameproofing mixture used.

As a desirable economy in any commercial application it would be necessary to reclaim the used retardant solution. It was found in the course of the Camp Lee experiments that satisfactory impregnation could be at-

tained by returning the reclaimed solution to the washer in sufficient amount to give the minimum 4-inch water level. Due to the dilution caused by the unextracted water in the garments, it was necessary to add a booster of the compound occasionally. The concentration of the retardant solution was readily checked by means of a hydrometer and a specific gravity table could be prepared for the particular compound or mixture used and serve in estimating the size of booster required. In the course of routine treatments by this type of procedure the amount of retardant required to renew the used solution could probably be determined on the basis of a few preliminary runs and remain essentially the same

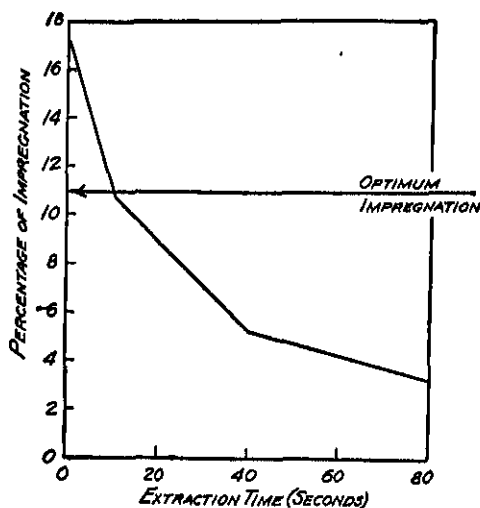


Figure 1. Relation of extraction time to percentage of impregnation. (Based on 28 pounds of retardant in a 4-inch water level.)

for subsequent treatments. A hydrometer reading would serve as a check of effective solution concentration.

Some of the available, commercially prepared, water-soluble flameproofing agents are quite acidic in nature and upon hydrolysis will exert a corrosive action upon equipment constructed of galvanized iron, copper, brass or bronze. Whenever possible, equipment made of stainless steel, lead, black iron, ceramic ware or wood should be used. In the event that the only equipment available is galvanized iron or one of the other metals which are subject to corrosion, it is necessary to flush out the washer and extractor after use. Washers made of galvanized iron were employed in the experiments described above and when properly flushed after use there were no signs of corrosive action on any of the laundry equipment.

As a result of the experiments described, the following technique was arrived at for flameproofing jackets, trousers and coveralls of 8.5-oz. herringbone twill. As was mentioned earlier the use of another flame retardant might necessitate a change in specific details such as the amount of compound used.

1. A wash-wheel load of clothing (55 to 60 lbs.) is first laundered ac-

according to the process previously described (2 suds and 3 rinses). Time—19 minutes.

2. The laundered clothing is then extracted for 3 minutes per 30-pound load. Time—6 minutes.

3. The washer is drained and capped. Time—3 minutes.

4. 28 pounds of the flame-retardant compound is placed in the washer which is filled to the 4-inch level and rotated for 5 minutes. Time—5 minutes.

5. The garments are placed in the washer, the water level readjusted to 4 inches and the washer run for 5 minutes. Time—6 minutes.

6. The clothing is extracted for 10 seconds per 30-pound load. (Centrifugal time is taken from the instant the starter button is pushed until the instant the stop button is pushed. The extractor is then slowed down and stopped by means of the foot brake.) Time—3 minutes.

7. With a setting of medium on the tumbler the clothing is tumbled until dry. Time—60 to 70 minutes.

8. The washer is drained, the solution reclaimed, and the washer flushed. Time—10 minutes.

The total time of operation for this technique, including the laundering, amounts to from 112 to 122 minutes. It is very probable that this time could be reduced somewhat using a permanent installation in a commercial laundry.

As an illustration of the possible adaptations of this type of process to commercial laundry practice, a flow sheet of a flameproofing technique for use with water-soluble flame retardants is presented in Figure 2.

B. DURABLE TREATMENTS

In recent years, the balance of interest in flameproofing treatments for textile materials has been centered upon those processes which display a greater or less degree of permanence. This has been heightened by the adaptation of flameproofing methods to commercial finishing practices and by the impending restrictions of the sale of hazardously inflammable fabrics. The three outstanding examples of durable flameproofing processes are thoroughly discussed in the following pages. The separation into the three general types shown was based partially on the nature of the flameproofing components themselves and, in part, upon the specific application techniques employed in industrial processing.

1. UREA-PHOSPHATE TYPE

a. Fundamentals of Processes

S. Coppick and William P. Hall

(1) Reaction Mechanisms

From purely fundamental considerations, the mineral acids have been shown to be singularly effective in inhibiting the combustion of cellulose.

This has led to considerable experimentation in the development of practical methods of adding these acid components to cellulosic materials. The addition of the simpler salts has already been discussed under "Temporary Treatments" in Section A of this chapter. In addition to the ammonium salts we may mention here other salts of organic bases such as urea,^{3,4} alkylolamines,⁵ guanidine,⁶ and dieryandiamide.^{7,8} The advantages of the amino or amido forms over the simple acid lie in the reduction of degradation through a buffering action and the ease of condensability to form complexes of lesser solubility.

Since the protection afforded by this type of treatment is primarily temporary in nature, attempts have been made to increase the permanence either by binding the acid or nitrogen-salt radical indirectly to the cellulose via resin condensation^{9,10} or by direct chemical combination with the cellulose itself. The acidic constituents in the former case may be sulfates, borates, or phosphates, while in the latter case the sulfates and phosphates are usually employed. From practical considerations the phosphates have been shown to be most effective in promoting the desirable flame and glow resistance in the treated fabric.

The heating of cellulose in the presence of an acidic substance together with a hydrogen acceptor and a swelling medium is well known to favor esterification and the existence of cellulose phosphate has been reported quite frequently in the recent literature.^{11,12,13,14,15,16} In general the reactions involved in the formation of the phosphate ester are impractical for flameproofing considerations due to the excessive degrading influence exerted on the fabric and the difficulty in adapting the solutions and methods used to commercial processes.

Recently, however, processes have been developed in which formation of the cellulose ester or nitrogen salt may be accomplished under conditions which are commercially practical and which do not excessively impair or destroy the fibrous properties of the cellulose.

Essentially, these processes involve treating the fiber at elevated temperatures with a mixture of an acid with a nitrogen compound. Under

³ Boller, E. R., U. S. Pat. 2,097,509 (Nov. 2, 1937).

⁴ Cupperry, M. E., U. S. Pat. 2,212,152 (Aug. 20, 1940).

⁵ Whitehead, W., U. S. Pat. 2,032,605 (Mar. 3, 1936).

⁶ Rosser, C. M., U. S. Pat. 2,305,035 (Dec. 15, 1942).

⁷ Triggs, British Pat. 476,043 (Oct. 31, 1936).

⁸ British Pat. 486,766 (June 7, 1938).

⁹ Groebe, F., U. S. Pat. 2,089,697 (Aug. 10, 1937).

¹⁰ Thomas and Houston, British Pat. 446,379 (Apr. 29, 1936).

¹¹ Dreyfuss, C., U. S. Pat. 1,837,150 (Dec. 15, 1931).

¹² Champetier, G., *Compt. Rend.*, 196, 930 (1933); *Ann. Chim.*, 10, 20, 5 (1933).

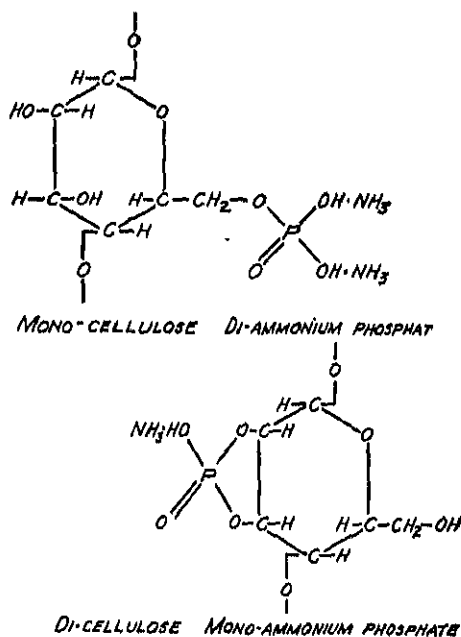
¹³ Tanner, W. L., U. S. Pat. 1,896,725 (Feb. 7, 1933).

¹⁴ Hagedorn, M., and Guehring, E., U. S. Pat. 1,848,524 (Mar. 8, 1932).

¹⁵ I. G. Farbenindustrie Akt.-Ges., German Pat. 547,812 (June 2, 1930).

¹⁶ I. G. Farbenindustrie Akt.-Ges., German Pat. 550,590 (June 4, 1930).

these conditions a combination takes place between the three constituents and a complex cellulose ester is formed. This imparts durable flame-resistant properties to the cellulose. The most convenient means for carrying out this reaction is first to immerse the fabric in an aqueous solution containing the acid and the organic base. After drying, the material is cured at elevated temperatures where the esterification proceeds and finally the fabric is washed to remove the excess and unreacted components. It is, of course, impossible to apply a strong inorganic acid to cellulose and



Molecular formulae for mono-cellulose di-ammonium phosphate and di-cellulose mono-ammonium phosphate.

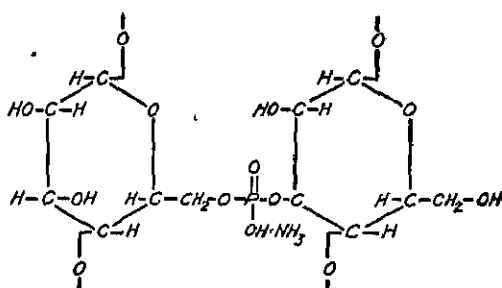
then to cure for prolonged periods of time at the temperatures required for esterification without completely disintegrating the fiber. It appears, however, that if a large excess of certain nitrogen compounds such as urea are present, the degradation is greatly reduced. Moreover, it also appears that the presence of the urea creates conditions which favor the esterification reaction.

Actually, the esterification takes place in a molten solution of the nitrogen compound containing the acidic component. Hence, at the temperatures employed anhydrous conditions exist and the removal of the water of reaction proceeds under favorable conditions. Although the constituents

are most conveniently applied from aqueous solution and dried on the fabric, the direct procedure of treating the cellulose with the molten solution leads to similar products.

The reaction of cellulose with acid phosphates in the presence of a nitrogen base may be presumed to occur as illustrated on page 182, to give the mono- or di- substituted ester existing as the nitrogen salt, which for convenience is illustrated as ammonia.

The mono-substitution may take place on either of the three available hydroxyls, but the primary (6) position should be the most readily esterified. With the di-substituted product the possibilities include reaction in the (2, 3) position as shown above, as well as between any one of the available hydroxyls on one cellulose chain together with another hydroxyl on a neighboring chain, i.e.:



Molecular formula for cross-linked di-cellulose phosphate.

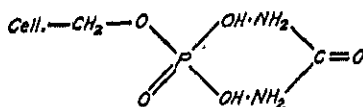
The analysis of a typical permanently flameproofed fabric is given in the following table:

Nitrogen:	2.48%
Calculated as urea	5.31
H ₃ PO ₄ :	8.78
Calculated as urea-phosphate	14.1
Add-on:	
Determined	16.0
Calculated as urea-phosphate	16.4
Mole ratio:	
H ₃ PO ₄ : urea	1.01 : 1
C ₆ H ₁₀ O ₅ : H ₃ PO ₄	5.92 : 1

This corresponds to an average degree of phosphorylation of about one ester group per 6 glucose anhydride units along the chain. The mean degree of substitution is hence about 0.16, but it should be pointed out that the reac-

tion is probably very far from homogeneous and high degrees of esterification will predominate in the more reactive locations on the fiber due to differences in morphological and fine structure.

The nitrogen content corresponds to two atoms of nitrogen per atom of phosphorus, and may be presumed to occur as either the cellulose ammonium phosphate or the cellulose urea phosphate, *i.e.*:



Molecular formula for cellulose urea phosphate.

(2) Reaction Variables

The practical formulations employed in these types of reactions are considerably more complex than those illustrated above; however, the general system involves:

- a. The cellulose.
- b. The polybasic acid.
- c. The salt-forming base.
- d. The swelling anhydrous reaction media.
- e. The buffer for the reaction.

In the simple system composed of phosphoric acid and urea, the phosphoric acid component serves the three functions listed in c, d and e. The following considerations may be given to the influence of variations in each constituent in more complex systems.

(a) Fabric Reactivity

The state of reactivity of the cellulose itself naturally dominates the case, extent and uniformity with which the esterification proceeds. The well-known factors influencing this activity are the kiering, desizing and mercerizing processes, all of which tend to produce a more receptive cellulose. Difficultly removable warp sizes or poor desizing pretreatment appears either to retard the esterification or at least decrease its efficiency.

(b) The Acidic Component

The acid constituent is preferably polybasic, which is in general agreement with the theories for the interchain bonding mechanism. The available acids meeting these specifications are those of phosphoric

sulfur, the former being the most efficient. It appears to be immaterial whether or not the original acid is in the higher or lower valance state so that metaphosphoric, orthophosphoric, pyrophosphoric, polyphosphoric, orthophosphorous and pyrophosphorous all behave similarly. However, orthophosphoric is usually employed. Since the reactive solution of the acid is sometimes prepared at elevated temperatures, and the esterification procedure itself is conducted between 150 and 200° C., the actual acidic component entering into the reaction with cellulose may not necessarily be that added as the primary component.

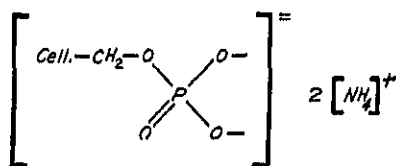
Substitution products of these acids may be employed provided that the substitution radical is of such a nature that it does not impair the rate of the esterification or reduce the hydrophilic nature of the ester. In general the introduction of groups of high carbon content reduces the efficiency of the acid as exhibited by the inferior protection afforded by fabrics prepared with either ethyl or phenyl phosphoric acid. Similarly, boron-substituted phosphoric acids lead to inferior products. Furthermore, it appears advisable to avoid unstable halogen-substituted phosphoric acids due to the excessive degradation encountered during curing or subsequent storage of the fabric. Thus fluorophosphoric is preferred to chlorophosphoric as the acidic component.

The hydrophilic nitrogen substitution products of the acids appear to be quite as satisfactory as the free acid itself. In any case the reactive mixture consists of an acid and a nitrogen base, and the acid does not exist entirely in the free state, but as the un-ionized salt in equilibrium with the corresponding ions. For example, diammonium orthophosphate, urea orthophosphate or guanidine pyrophosphate may be used in part or entirely in place of the acid. Similarly the amido acids such as phosphamic or the so-called nitrile hexaphosphoric are effective. The exact constitution of many of the nitrogen-containing phosphoric acids is still a controversial subject and many acids of unknown constitution may be formed by reacting together the acid, its oxide or oxychloride and nitrogen-containing compounds at elevated temperatures. These acids also are effective.

Metallie substitution products of the acids are generally considerably less efficient in their protective action than the free acid itself. For example, monosodium orthophosphate gives fair results while disodium and trisodium orthophosphate result in poor retardancy. Similarly, phosphates of the dibasic metals such as calcium and magnesium result in products with no appreciable flame resistance.

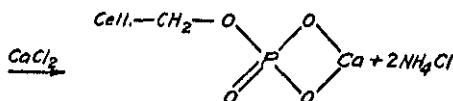
(c) *The Salt-Forming Base*

The effect of these various changes in the acid is readily explained on consideration of the ionic nature of the resulting ester salt. All of these structures are ionized salts and are more correctly represented as,



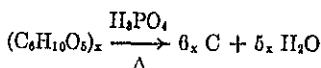
Molecular formula for ionized ammonium salt of cellulose phosphate.

and are capable of exchange with a metallic ion as follows:



Molecular equation for formation of calcium salt of cellulose phosphate.

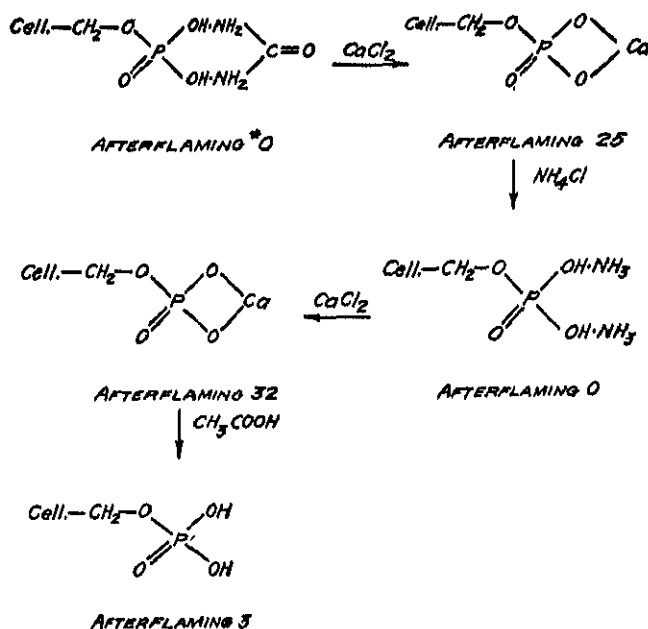
The resulting calcium salt is stable at flame temperatures and will produce phosphoric acid when heated, as will the ammonium salt. The flameproofing mechanism whereby cellulose is dehydrated on heating to promote formation of non-flaming products is thus destroyed by the exchange with alkaline earth metals. The proposed dehydration flameproofing mechanism may be represented as



rather than the normal decomposition whereby inflammable tars and gases are produced.

Similarly the interchain bonding capacity of the phosphate radical would be destroyed by replacement of the strongly hydrophilic carbonyl or amino groups with hydrophobic groups or metals not capable of fission at flame temperatures. The facts then are also in accord with this flameproofing mechanism as proposed by Sisson¹⁷ and previously outlined in Chapter III. Some phosphated fabrics behave typically as ion-exchange complexes, and may be conducted through a series of successive treatments whereby the protective qualities are lost and regained by addition or removal of the appropriate ion as shown below. These reactions may be illustrated as:

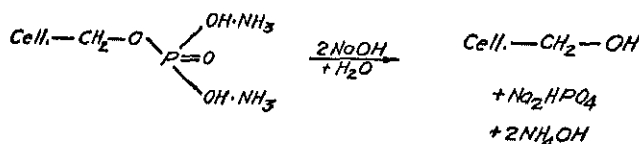
¹⁷ Sisson, W. A., Paper presented at Industrial Advisory Panel Meeting on Flameproofing, N.R.C. Project Q.M.C. # 27, Office of the Quartermaster General, Washington, D. C. (1945).



*AFTERFLAMING IN SECONDS VIA THE 45° MICROBURNER FLAME TEST.

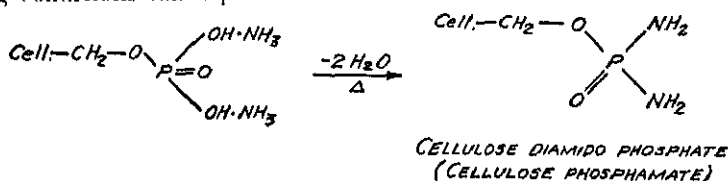
Molecular equations depicting ion-exchange reactions with CaCl_2 .

These hypotheses would explain also the instability of some phosphated fabrics to sea water and very probably account for the loss of fireproofing qualities during laundering with ionic detergents. With strongly alkaline detergents, however, the action most probably is mainly saponification, *i.e.*:



Molecular equation for saponification of cellulose ammonium phosphate

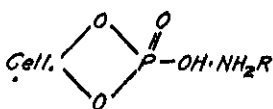
The prolonged heating of ammonium salts favors the formation of the non-ionic amide. It is hence proposed that increased stability by suitable curing conditions takes place as follows:



Molecular equation for formation of amide on heating via dehydration.

This latter structure should be stable to media such as sea water, ionic laundering conditions, etc., but still should be susceptible to saponification by strong alkali.

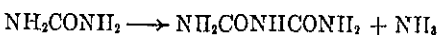
By appropriate formulation of the treating solution and by adjusting curing conditions the tendency towards ionic reactions of the type treated above may be decreased, quite appreciably. Besides the amidation as previously discussed, there exists the possibility of causing condensations to occur with the nitrogen salt radical to render it insoluble. Furthermore, the use of more complex amines or amides to increase the molecular size of the side group should also decrease diffusion and rates of exchange. These types may be illustrated as:



Type formula for complex cellulose phosphate amides and amines.

where R may be considered as an —N—C(=O)— complex. The increasing nitrogen to phosphorus ratio in the more permanent fabrics discussed in the following sections illustrates this behavior.

The nitrogen base used in the treatment controls the type of nitrogen salt of the cellulose ester. However, since the curing conditions may be above dissociation and condensation temperatures, the resultant may not be that of the original base. For example, in processes involving urea, the following proceeds during curing:



Thus we have the possibility for formation of either the urea, biuret, or ammonium salt. Moreover, in complex systems involving several nitrogenous compounds the number of possibilities are enormous and the system becomes very complicated. Further complications are introduced when one considers the number of possible combinations and condensations which can occur upon heating, say, urea and guanidine in the presence of anhydrous phosphoric acid. Moreover, on the final washing of the cured fabric, ion exchange reactions occur and in the limit the final structure will probably be determined by the most stable of the salts present and its concentration at the surface.

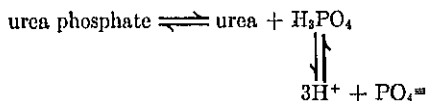
(d) *The Reaction Medium*

To carry out the reaction at the temperature required for the esterification a medium is necessary. The requirements for this are that it should be a solvent for the acid component and a swelling agent for the cellu-

That is, it should distend the disordered regions of the network to an extent at least equal to that produced by water and transport the esterification agent into the fiber. The medium should be fluid in the anhydrous state at temperatures above 140° C. and as far as possible should be chemically inert towards cellulose. Moreover, it should not decompose readily at curing temperatures to give highly basic or acidic substances for obvious reasons. The substances which come closest to satisfying all these requirements are the weak nitrogen bases with strong hydrogen bonding groups. These groups must be stronger than the mutual attraction between the cellulosic hydroxyls which naturally leads to the choice of the >C=O and —NH_2 radicals. Thus the reaction proceeds in the presence of formamide, acetamide, urea, biuret, dicyandiamide, or melamine. Substitution products of these weak nitrogen bases may be used as media provided the substitution does not destroy or reduce their hydrophilic or hydrogen bonding power. Halogen, alkyl or aryl substitution products appear to be unsatisfactory as exemplified by the relatively poor performance of methyl urea. Moreover, the weak basic character of the media should not be altered by the introduction of amino or hydroxy groups as, for instance, in imino-urea (guanidine) which develops strong basic characteristics in the process.

(c) *The Reaction Buffer*

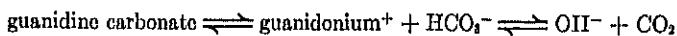
The esterification appears to proceed most satisfactorily under acidic conditions, but these are also the conditions under which hydrolytic degradation ensues with unfavorable strength losses. Moreover, as pointed out in Chapter II, in the alkaline range oxidative processes occur which are equally detrimental to the physical properties of the final product. It is obvious therefore that the reaction should be carefully buffered at optimum conditions which favor a sufficiently rapid esterification with a minimum degradation. Of all the substances which appear to protect cellulose at high temperatures, urea appears to be the most satisfactory. Furthermore, the system



assumes a pH in the presence of excess urea of such a value that the ideal is closely approximated. This buffer appears to have a wide concentration range of fairly constant acidity and also has a favorable tolerance to temperature variations. Similar conditions result in some of the other media discussed above, but urea appears to be the best. For example, substantial changes may be made in the treating solution containing urea without appreciably altering the solution pH or the cured cloth pH. How-

ever, when similar changes are made in a system involving guanidine wide variations in pH occur, and if the guanidine is in excess the solution may become so decidedly basic that esterification is markedly retarded and degradation accelerated.

However, it is advantageous to employ certain of the stronger nitrogenous bases in conjunction with an excess of a weaker buffering base. Thus the following system



is also buffered by excess urea at a pH slightly higher than that occurring in the absence of the guanidine carbonate. The mixed system seems to be preferable from the standpoint of tolerances in reaction control and stability of the products. Similar behavior is exhibited by dihydroxyguanidine, guanylurea, aminoguanidine and biguanide. However, since these are all strong bases they are limited to use in the presence of an excess of a buffer such as urea. When such mixed systems are used the resulting ester exists principally as the salt of the stronger base, since nitrogen to phosphorus ratios are increased. The complexity and stability of these salts favors durability and the products are less susceptible to ion-exchange during leaching and laundering.

b. Laboratory Impregnations

Robert W. Little

In the preceding section an attempt has been made to acquaint the reader with the underlying principles governing the effectiveness and permanence of the urea-phosphate type of flameproofing treatment. The description of actual laboratory investigations contained in the following pages serves to illustrate and substantiate the theoretical considerations. It should be borne in mind that the fundamentals considered are equally applicable regardless of the specific nature of the acid or amide employed in any particular instance.

Reaction Components. Considering the simplest possible system, a mixture of urea and phosphoric acid, it may be well to review briefly the primary function of each of the components. As indicated in previous sections, the flameproofing ingredient in these systems is the inorganic acid or its ammonium salt. Ultimately the effects may be traced to the acid anhydride itself. The amide or related compound included is intended to serve in the capacity of a solvent for the reaction between the two solid reactants and function in both the reduction of the tendering which accompanies the reaction and the formation of simple or complex amido salts which tend to increase the permanence of the treatment. The flame-resistant characteristics of the separate components are demonstrated by the data of Table 3. Obviously, urea by itself has no significant effect upon

Table 3. Performance of the Separate Components of the Urea-Phosphate Treatment (Vertical-Bunsen Flame Test)

Material Added	Add-On %	Aftertreatment	Afterflame sec.	Afterglow sec.	Char Length in.
Urea	14.6	air dried	25	110	C.B.*
		leached 30 min., tap water	25	80	C.B.
		cured 15 min., 160° C	27	91	C.B.
		cured and leached	24	90	C.B.
Phosphoric Acid	14.8	air dried	0	0	3.7
		leached 30 min., tap water	25	5	C.B.
		cured 15 min., 160° C	0	1	3.5
		cured and leached	14	0	B.E.**
Urea: Phosphoric Acid (1 : 1)	12.5	air dried	0	0	3.2
		leached 30 min., tap water	25	40	C.B.
		cured 15 min., 160° C	0	0	3.9
		cured and leached	0	0	4.4

* C.B.—Completely burned.

** B E.—Burned to the end.

the resistance of the fabric to either afterflaming or afterglow. Orthophosphoric acid alone is an effective flameproofing agent but cannot be cured into the fabric to produce a permanent retardancy. An equal mixture of the two, on the other hand, imparts a high degree of flameproofness to the fabric which, when cured, is resistant to leaching.

The inclusion of additional components in the formula is intended to enhance the permanence of the retardancy and prevent, insofar as possible, the loss of fabric strength. The data presented in Table 4 show that the acidity of the impregnating solution is reduced practically to neutral by the addition of ammonium hydroxide. It is apparent, however, that the pH of the treating mixture is not the governing factor in the strength loss which occurs. The loss in strength with an initial solution pH of 1.5 is not appreciably greater than that occurring when the solution has a pH of 8.3. The deterioration of fabric strength is therefore closely associated with the actual reaction between cellulose and phosphoric acid. Apparently the majority of the loss in strength occurs within the first few minutes of the curing period. Continued curing beyond this point does not produce corresponding reduction in fabric strength but, as will be seen shortly, is essential in bringing about the salt formation and cross linkage required for permanence. The addition of formaldehyde does exert some protective action on the strength characteristics, which is due at least in part to the formation of a urea-formaldehyde resinous coating. Coincident with the gain in residual strength, however, is a reduction in the ability of the treated fabric to resist the ion-exchange tendencies of solutions containing alkali or alkaline earth ions. As seen in Figure 3, increasing the amount of formaldehyde in the impregnating bath appreciably reduced the re-

Table 4. Effect of the Addition of Ammonium Hydroxide and Formaldehyde in Preventing the Loss of Fabric Strength During the Cure

Impregnating Solution	Urea + Phosphoric Acid Unheated	Urea + Phosphoric Acid Heated to 190° C.	Urea + Phosphoric Acid + Ammonium Hydroxide	Urea + Phosphoric Acid + Ammonium Hydroxide + Formaldehyde
	Min. at 150° C.			
pH	1.5	6.0	8.3	7.6
Add-On %	16.0	17.5	17.5	12.0

Cure Time		Warp Tensile Strength, lbs./in. (1-inch strip test)	
Min. at 150° C.			
0	109	109	109
15	56	68	85
20	64	68	78
25	63	64	83
30	66	62	81

Table 6. Ion-Exchange Reactions of a Commercial Urea-Phosphate Type Fabric (45°-Microburner Flame Test)

Leaching Solution	Flameproofness after 30 min. boil in leaching solution, followed by 15-min cold water leach and drying		Flameproofness after boiling, leached specimen in 5% ammonium chloride for 30 min., followed by 15-min cold water leach and drying	
	Afterflame sec.	Afterglow sec.	Afterflame sec.	Afterglow sec.
None	0	0	—	—
Water	0	0	0	0
5% Sodium chloride	2	0	0	0
5% Calcium chloride	60	0	0	0
5% Magnesium sulfate	58	0	0	0
Synthetic sea water	55	0	0	0
			Char Area in ²	Char Area in ²
			3.1	—
			3.3	3.7
			6.8	3.7
			B.E.*	4.5
			B.E.	5.5
			B.E.	5.1

* B.E.—Burned to the end

sistance of the treated fabric to leaching in calcium chloride solutions. This might be attributed to a competition between the formaldehyde and phosphoric acid or cellulose phosphate ester for the urea available. The more of the amide that is tied up by the formaldehyde present, the less

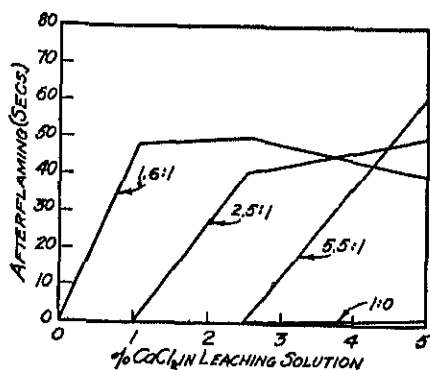


Figure 3. Effect of the addition of formaldehyde on the permanence of urea-phosphate treated fabrics. (The curves are for different ratios of urea: formaldehyde.)

is available for the formation of amido-type derivatives of the cellulose phosphate.

Fabric Degradation. Further evidence that the strength loss accompanying the flameproofing treatment is attributable to the combination of cellulose with the acid added is furnished by the data of Table 5. Expo-

Table 5. Effect of Time of Cure Upon the Tensile Strength of Fabric Treated with Urea-Phosphoric Acid

	Cure Time Min. at 140° C.	Warp Tensile Strength lbs./in. (1-inch strip test)
Untreated	0	113
	15	101
	30	107
	45	103
	60	112
Treated	2	76
	4	75
	6	72
	8	68
	10	61
	15	60

sure of untreated fabric to the same curing conditions produces no significant decrease in the tensile strength. In this case it is apparent that, although the majority of the tensile loss suffered occurs in the first two minutes of the curing period, prolonging the exposure progressively degrades the fabric though at a much slower rate.

Resistance to Ion-Exchange. As emphasized in the preceding fundamental considerations, the ion-exchange phenomena are of vital importance with respect to this type of flameproofing process. This is readily

illustrated by a series of experiments of the type summarized in Table 6, showing the ease with which the amido salts of the cellulose-phosphate ester may be destroyed by leaching in high concentrations of sodium, calcium or magnesium ions. That the reaction involved is truly an ion-exchange is further substantiated by the recovery of flameproof characteristics when the ammonium salt of the ester is formed by leaching the impoverished fabric in a solution of ammonium chloride. The proof of the actual removal and re-addition of nitrogen is offered by the analytical data recorded in Table 7. The nitrogen content of the fabric is reduced

Table 7. Changes in Composition of a Commercial Urea-Phosphate Type Fabric Produced by Ion-Exchange Reactions

Successive Treatments	Nitrogen Content % N	Phosphorous Content % H_3PO_4	Molar Ratio N : H_3PO_4
None	2.23	8.97	1.78
30-min. boil in 5% calcium chloride, 15-min. cold water leach, dried 15 min. at 100° C.	0.48	7.39	0.45
30-min. boil in 5% ammonium chloride, 15-min. cold water leach, dried 15 min. at 100° C.	1.21	7.07	1.21

to practically one-fifth by the leaching in calcium chloride solution. Subsequent formation of the ammonium salt does not rebuild the nitrogen content to its former value but does replace sufficient nitrogen to raise the N/H_3PO_4 ratio above 1. The stability of the phosphate linkage to cellulose is demonstrated by the extent to which the phosphate content is retained throughout the leaching treatments. The resistance of the treated fabric to ionic transfers has been stated to be proportional to the amount of urea present in the impregnating solution and the extent to which it is converted to biuret, cyanuric acid and the melamines. Investigations of the influence of the urea:diammonium phosphate ratio in the solution upon the permanence of the resulting treatment illustrate this point. Fabric specimens impregnated with mixtures of these two materials in varying ratios were air-dried and then cured for 15 minutes at 150° C. For the sake of simplicity these treated fabrics are termed UDAP fabrics, employing a contraction of the components urea and diammonium phosphate. The results of this series of experiments are presented in Table 8 showing the relative strengths of the treated fabrics and their flameproofness after exposure to leaching conditions of varying severity. In this case, the strength of the fabric is only very slightly improved by incorporation of greater amounts of urea in the mixture. The effect upon the resistance to exchange with calcium ion is very apparent, however, and only with urea:phosphate ratios in the order of 4.4:1 molar, is the

Table 8. Effect of Increased Ratios of Urea : Diammonium Phosphate on the Resistance of UDAP Fabrics to Ion-Exchange
(45°-Microburner Flame Test)

Molar Ratio Urea: Diammonium Phosphate	Warp Tensile Strength lbs./in. (strip)***	Leaching Solution	After- flame sec.	After- glow sec.	Char Area in ²
0 : 1	—	Cold water	51	0	C.B.*
0.22 : 1	52	Cold water	46	0	C.B.
		Hot water	72	0	C.B.
0.44 : 1	69	Cold water	0	0	4.6
		Hot water	40	0	B.E.**
1.1 : 1	66	Cold water	0	0	2.4
		Hot water	0	0	4.1
		1% Calcium chloride	34	0	B.E.
		2.5% Calcium chloride	57	0	B.E.
		5.0% Calcium chloride	63	7	B.E.
2.2 : 1	59	Cold water	0	0	2.4
		Hot water	0	0	3.6
		1% Calcium chloride	0	0	4.8
		2.5% Calcium chloride	0	0	5.1
		5.0% Calcium chloride	33	0	B.E.
3.3 : 1	61	Cold water	0	0	2.2
		Hot water	0	0	3.6
		1% Calcium chloride	0	0	3.9
		2.5% Calcium chloride	0	0	4.1
		5.0% Calcium chloride	3	0	3.9
4.4 : 1	62	Cold water	0	0	2.2
		Hot water	0	0	2.3
		1% Calcium chloride	0	0	3.0
		2.5% Calcium chloride	0	0	3.5
		5.0% Calcium chloride	0	0	3.6

* C.B.—Completely burned.

** B.E.—Burned to the end.

*** Tensile strength of untreated fabric = 100–130 lbs./in.

treatment capable of resisting immersion in the 5% calcium chloride solution. With approximately a 1:1 molar ratio the fabric is just able to withstand a 30-minute immersion in boiling water. It is apparent, therefore, that in order to achieve permanent flameproofness it is not sufficient that there be only enough of the amide present to form a urea-phosphate salt but that an excess must be available to permit polymerization to cyanuric acid and melamine derivatives. Further reason for requiring an excess of urea is the loss which is incurred due to volatilization during the curing process.

Effect of Other Acids and Amides. According to fundamental considerations either of the components of the urea-phosphate system may

be replaced by materials of similar chemical nature. Substitutions of urea have been made using higher molecular weight amides such as dicyandiamide and the dicyanoguanidines. Similarly, orthophosphoric acid and its ammonium salts have been replaced by pyrophosphates, phosphamates and sulfamates. The theoretical considerations are similar in each case but the actual conditions required for effective treatment may vary widely. To serve as an illustration, data on a series of fabrics treated with urea-phosphate, urea-sulfamate, urea-sulfamate-phosphate and dicyandiamide phosphate have been assembled in Table 9. In each case the fabric speci-

Table 9. Effect of Replacement of Urea and Phosphate with Other Similar Compounds
(45°-Microburner Flame Test)

Treating Mixture % by Wt.	Solution Conc. %	Warp Tensile Strength lbs./in. (strip)***	Successive Leaching Treatments	Add- On %	After- flame sec.	After- glow sec.	Char Area in ²
Urea :			Cold water	15.0	0	0	3.5
Diammonium			Hot water	11.6	0	0	3.8
Phosphate	46	63	30 min., sea water	—	3	0	3.9
(2 : 1)			60 min., sea water	—	3	0	5.2
			90 min., sea water	—	28	0	6.8
Urea :			Cold water	9.8	0	0	2.5
Ammonium			Hot water	8.0	0	0	4.5
Sulfamate :	46	67	30 min., sea water	—	43	250	B.E. *
Diammonium			60 min., sea water	—	46	550	B.E.
Phosphate			90 min., sea water	—	48	700	B.E.
(20 : 7 : 3)							
Urea :			Cold water	7.3	27	0	B.E.
Ammonium			Hot water	4.8	40	600	B.E.
Sulfamate	46	87	30 min., sea water	—	63	> 300	B.E.
(2 : 1)			60 min., sea water	—	58	> 300	C.B. **
			90 min., sea water	—	63	> 300	C.B.
Dicyandiamide:			Cold water	—	0	0	2.8
Diammonium			Hot water	—	0	0	3.9
Phosphate	46	—	30 min., sea water	—	—	—	—
(2 : 1)			60 min., sea water	—	—	—	—
			90 min., sea water	—	—	—	—
Dicyandiamide:			Cold water	—	0	0	3.0
Diammonium			Hot water	—	0	0	3.8
Phosphate	36.4	79	30 min., sea water	—	65	0	B.E.
(1 : 1)			60 min., sea water	—	68	0	B.E.
			90 min., sea water	—	70	0	B.E.
Dicyandiamide :			Cold water	—	0	0	3.1
Diammonium			Hot water	—	0	0	3.4
Phosphate	30.8	83	30 min., sea water	—	43	0	B.E.
(1 : 2)			60 min., sea water	—	47	0	B.E.
			90 min., sea water	—	43	0	B.E.

* B.E.—Burned to the end.

** C.B.—Completely burned.

*** Tensile strength of untreated fabric = 100-130 lbs./in.

mens were cured for 15 minutes at 140° C. These curing conditions are sub-optimum but serve in this instance to better illustrate the differences in permanence encountered. It is apparent that the substitution of ammonium sulfamate for the phosphate is advantageous in the prevention of tendering but that the retardant is not as readily cured into the fabric and as a result tends to produce low add-on fabrics possessing a much lower degree of permanence. The same is true of the mixture wherein dicyandiamide replaces urea in conjunction with diammonium phosphate. In order to achieve comparable effectiveness and permanence with these substitution mixtures it is necessary to increase the severity of the cure with respect to the time or temperature or both. This is further illustrated by the data of Table 10, comparing the effect of the time of cure upon the add-on and

Table 10. Effect of Time of Cure Upon the Permanence and Strength of Urea-Phosphate and Urea-Sulfamate Treated Fabrics — Sea Water Resistance
(45°-Microburner Flame Test)

Treatment	Cure Time min.	Add-On %	Warp Tensile Strength lbs./in. (strip)***	Time in Sea Water min.	After-flame sec.	After-glow sec.	Char Area in ²
Urea :	5	5.1	80.5	0	0	0	4.1
Diammonium Phosphate;				60	50	45	B.E.*
2 : 1 by wt.				120	57	2	B.E.
46 % solution							
Cured at 140° C.	10	14.1	66.5	0	0	0	2.0
				60	38	0	B.E.
				120	39	0	B.E.
	15	15.6	68.5	0	0	0	2.5
				60	2	0	2.8
				120	0	0	2.9
	20	16.8	68.2	0	0	0	2.1
				60	0	0	3.1
				120	0	0	3.0
	25	18.0	62.7	0	0	0	2.2
				60	0	0	2.9
				120	0	0	2.7
	30	19.1	57.2	0	0	0	2.1
				60	0	0	2.4
				120	0	0	2.4
	40	20.5	57.5	0	0	0	2.2
				60	0	0	2.6
				120	0	0	2.4
	50	19.3	60.5	0	0	0	1.9
				60	0	0	2.1
				120	0	0	2.2
	60	19.4	60.5	0	0	0	2.2
				60	0	0	2.2
				120	0	0	2.0

(Continued on next page)

Table 10. Effect of Time of Cure Upon the Permanence and Strength of Urea-Phosphate and Urea-Sulfamate Treated Fabrics — Sea Water Resistance (*Continued*)
(*45°-Microburner Flame Test*)

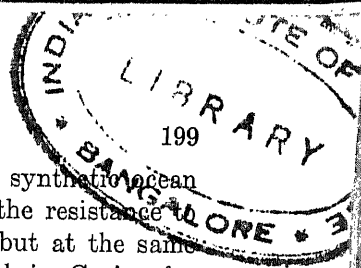
Treatment	Cure Time min.	Add-On %	Warp Tensile Strength lbs./in. (strip)***	Time in Sea Water min.	After-flame sec.	After-glow sec.	Char Area in ²
Urea :	5	1.6	88	0	58	185	C.B.**
Ammonium Sulfamate;				60	47	>300	C.B.
2 : 1 by wt.				120	52	120	C.B.
46% solution							
Cured at 140° C.	10	4.2	88	0	38	562	B.E.
				60	73	>300	C.B.
				120	63	>300	C.B.
	15	7.3	87	0	27	0	B.E.
				60	58	>300	C.B.
				120	58	>300	C.B.
	20	10.2	88	0	0	0	4.0
				60	53	195	B.E.
				120	48	>300	B.E.
	25	9.9	88	0	0	0	4.5
				60	48	>300	B.E.
				120	55	>300	C.B.
	30	12.3	79	0	0	0	4.0
				60	38	>300	B.E.
				120	38	>300	B.E.
	40	15.8	81	0	0	0	3.1
				60	5	>300	4.5
				120	2	>300	4.8
	50	18.9	77	0	0	0	3.3
				60	4	>300	4.2
				120	0	>300	4.7
	60	23.5	74	0	0	0	3.0
				60	3	>300	4.6
				120	0	152	4.3

* B.E.—Burned to the end.

** C.B.—Completely burned.

*** Tensile strength of untreated fabric = 100–130 lbs./in.

permanence obtained with the urea-phosphate and urea-sulfamate treatments. An effective and permanent treatment is obtained with the urea-phosphate system on curing for 20 minutes at 140° C. Additional curing beyond this point does not produce appreciable changes in the add-on, strength or flameproofness of the fabric. With urea-sulfamate, curing for 20 minutes at 140° C. again produces a fabric possessing good initial flameproofness and a residual fabric strength superior to the phosphate mixture. The add-on obtained is appreciably lower, however, and the effec-



tiveness of the retardancy is destroyed by immersion in synthetic ocean water. Increasing the time of cure in order to improve the resistance to ion-exchange, produces correspondingly higher add-ons but at the same time progressively reduces the strength of the treated fabric. Curing for as long as 60 minutes at 140° C. does not result in a permanence comparable to that obtained in the case of the phosphate with a 20-minute cure, in spite of the fact that the add-on is 50% greater. In other words, it is very probable that the production of a comparable fabric with the urea-sulfamate mixture by increasing the severity of the cure conditions would result in a fabric of appreciably higher add-on and very nearly the same tensile strength. It would appear therefore that variations in the con-

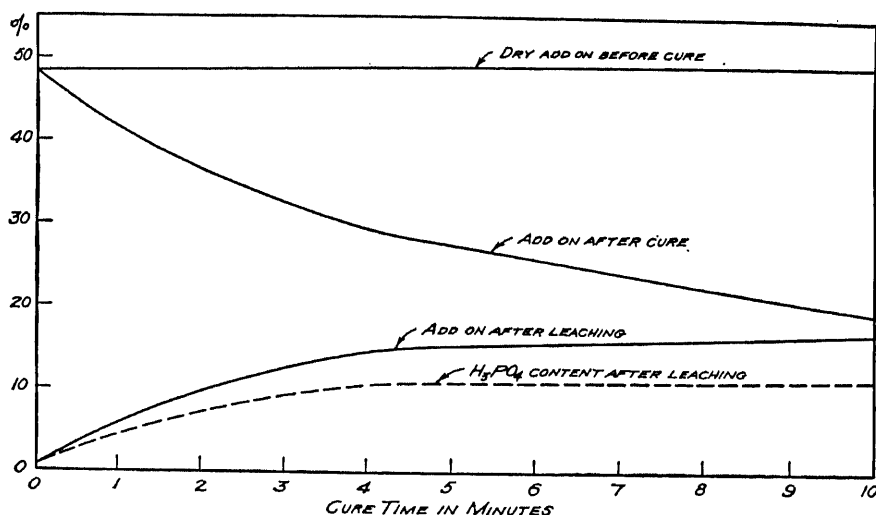


Figure 4. Fixation of urea-phosphate on curing (180° C.).

stituents employed in order to retain a maximum amount of strength in the treated fabric would produce a corresponding increase in the final add-on or decrease in the resistance of the processed fabric to ionic transfer. In view of the above and for the sake of simplicity the remaining considerations will be restricted to the simple system of urea and diammonium phosphate.

Nitrogen to Phosphate Ratio. The changes occurring in the amount of material added to the fabric and the composition of the mixture are illustrated by the data of Table 11 and the curves of Figure 4. Progressive curing is shown to produce a gradual sublimation of urea and fixation of phosphate in the fabric. Since the phosphate represents the primary flameproofing ingredient, it is apparent that in order to achieve an effective flameproofing treatment, the cure must be continued until the flat portion

Table 11. Variation of Phosphate Content and Permanence with Time and Temperature of Cure
(45°-Microburner Flame Test)

Cure Temp., °C	Cure Time min.	Warp Tensile Strength lbs./in. (strip)	Dried	Add-On % Cured	Leached	H ₃ PO ₄ (leached)	30-Min. After-flame sec.	Water Leach After-glow sec.	Char Area in ²	2-Hr. After-flame sec.	Water Leach After-glow sec.	Char Area in ²
—	0	103	48.6	—	—	11.8*	0	0	2.4.*	—	—	—
—	0	103	47.8	—	0.6	0.6	90	17	B.E.	—	—	—
160	2	104	43.1	39.7	0	0.5	104	0	B.E.	67	183	B.E.**
	4	86	46.9	37.1	9.9	6.0	0	0	2.9	56	0	B.E.
	6	81	51.0	34.7	13.9	8.8	0	0	2.9	48	0	B.E.
	8	79	52.2	32.4	18.6	8.4	0	1	3.0	0	0	2.7
	10	77	51.0	28.0	15.5	9.0	0	1	2.5	39	0	B.E.
	12	73	48.2	23.9	14.7	8.4	0	1	2.8	0	0	2.7
	14	69	48.3	23.9	13.6	9.3	0	0	2.1	0	0	2.7
	16	67	47.6	21.3	14.7	8.9	0	0	2.3	36	0	B.E.
	18	69	48.9	21.3	15.2	8.6	0	0	2.2	42	0	B.E.
	20	70	48.0	20.3	13.4	8.6	0	0	2.2	41	0	B.E.
170	2	98	49.8	43.3	3.1	2.9	49	0	B.E.	63	47	B.E.
	3	85	48.8	36.9	8.6	6.5	0	1	2.7	57	0	B.E.
	4	83	51.3	35.1	11.9	8.7	0	0	2.1	35	0	B.E.
	5	78	48.7	29.7	13.3	10.0	0	0	2.2	44	0	B.E.
	6	76	49.0	28.8	13.3	10.0	0	0	2.3	0	0	2.8
	7	74	48.4	26.2	14.1	10.5	0	0	2.2	34	0	B.E.
	9	73	48.7	23.3	14.5	11.1	0	0	2.4	36	0	B.E.
	11	71	49.7	21.8	16.7	10.4	0	0	2.3	33	0	B.E.
	13	66	49.1	20.9	16.5	8.9	0	0	2.5	0	0	2.7
	15	66	49.8	19.5	16.8	9.6	0	0	2.4	0	0	2.7

*—These specimens were not leached.

** B.E.—Burned to the end.

(Continued on next page)

Table 11. Variation of Phosphate Content and Permanence with Time and Temperature of Cure (Continued)
(45° Microburner Flame Test)

Cure Temp. ° C.	Cure Time min.	Warp Tensile Strength lbs./in. (strip)	Dried	Add-On % Cured	Leached	% HfO ₂ (Leached)	30-Min. After- flame sec.	Water Leach After- glow sec.	Char Area in ²	2-Hr. After- flame sec.	Sea Water After- glow sec.	Char Area in ²
180	2	85	47.1	38.7	8.2	4.9	0	1	3.7	46	0	B.E.**
	3	84	44.3	30.0	12.6	8.8	0	1	2.8	43	0	B.E.
	4	80	47.8	30.3	14.0	10.1	0	1	2.5	45	0	B.E.
	5	76	50.2	26.8	14.9	10.2	0	1	2.6	39	0	B.E.
	6	72	48.9	24.8	15.6	10.3	0	0	2.2	0	0	3.3
	7	72	48.9	23.0	15.1	9.9	0	0	2.8	2	0	3.1
	8	67	48.4	20.3	14.2	10.1	0	1	2.8	0	0	2.6
	9	66	49.5	19.8	15.4	9.9	0	1	2.9	0	0	2.8
	10	64	48.2	18.8	15.4	10.3	0	0	2.8	0	0	2.9

** B.E.—Burned to the end.

Table 12. Effect of Nitrogen Content and Nitrogen : Phosphoric Acid Ratio Upon the Permanence of Urea-Phosphate Treated Fabrics

Dry	Add-On Cured	% Leached	Analysis after 30-Min. Water Leach			Analysis after 2-Hr. Sea Water Leach			Flameproofness after Sea Water (45°-Microburner Test)		
			% H ₃ PO ₄	% N	$\frac{N}{H_3PO_4}$ (molar)	% H ₃ PO ₄	% N	$\frac{N}{H_3PO_4}$ (molar)	After- flame sec.	After- glow sec.	Char Area in ²
(Cured 30 min. at 140° C.)											
57.0	34.0	17.3	11.1	2.2	1.4	5.4	0.49	.58	0	0	2.3
									41	0	B.E.*
55.5	32.3	17.5	11.6	2.1	1.3	5.6	0.51	.59	45	0	B.E.
									45	0	B.E.
54.5	27.4	17.7	12.1	2.3	1.3	6.4	0.66	.69	0	0	2.5
									44	0	B.E.
53.7	33.6	16.8	11.4	2.3	1.4	6.1	0.54	.63	0	0	2.2
									46	0	B.E.
55.0	33.4	15.2	11.2	2.6	1.6	6.2	0.51	.57	43	0	B.E.
									49	0	B.E.
53.5	32.4	15.2	11.6	2.3	1.4	6.2	0.49	.56	50	0	B.E.
									48	0	B.E.
(Cured 15 min. at 180° C.)											
47.2	20.0	15.9	11.5	2.3	1.4	8.1	1.0	.85	38	0	B.E.
									0	1	2.5
47.0	19.6	15.9	10.6	2.2	1.4	8.5	0.9	.77	0	2	2.5
									0	1	2.4
47.5	19.8	16.5	10.4	2.9	1.9	9.5	1.0	.72	0	1	2.6
									0	0	2.8
48.2	20.3	16.3	11.1	2.6	1.6	9.2	0.9	.71	0	0	2.5
									0	0	2.7
48.3	20.4	16.6	10.4	2.4	1.7	9.4	1.0	.73	0	1	2.4
									0	1	2.6
46.6	19.9	16.6	11.7	2.4	1.4	9.2	0.9	.68	38	0	B.E.
									39	0	B.E.
(Cured 10 min. at 190° C.)											
49.3	18.5	14.4	12.6	2.1	1.2	6.9	1.0	1.08	0	0	2.8
									0	0	2.5
49.0	18.0	14.2	9.5	2.1	1.6	6.9	1.0	1.08	0	0	2.8
									0	0	2.6
50.4	19.1	14.9	9.5	2.3	1.7	6.7	1.2	1.30	0	0	2.8
									0	0	2.5
49.7	18.1	14.5	9.5	2.3	1.7	6.3	1.0	1.11	0	0	2.8
									0	0	2.5
49.3	16.6	14.4	12.0	2.3	1.3	6.8	1.1	1.12	0	0	2.6
									0	0	2.6
49.1	16.7	14.5	12.2	2.4	1.4	6.2	1.0	1.12	0	0	2.7
									0	0	2.5

* B.E.—Burned to the end.

of the add-on or phosphate content curves have been reached, or until a maximum fixation of phosphate has been accomplished. As shown by the flame test data of Table 11, however, this insures an adequate initial flameproofness but does not guarantee a permanent retardancy. The phosphate content alone does not represent the governing factor in the resistance of the fabric to leaching action. Many of the fabrics showing poor resistance to ion exchange contain the required amount of phosphate, which appears to be in the order of 9 to 10%. As previously discussed, the permanence of the treatment is more dependent upon the degree of salt formation and the extent of the polymerization and cross linkage of the amide. The permanent flameproofness, therefore, should be proportional, not to the phosphate content, but rather to the nitrogen to phosphate ratio. This is well illustrated by the data presented in Table 12. When the cure is insufficient to produce the required fixation of the nitrogen-bearing component, the sea water leach results in appreciable loss of nitrogen and the N/H_3PO_4 ratio is reduced from approximately 1.4 to the order of 0.63. In the majority of cases these treated fabrics lose their flame-resistant characteristics at the same time. With an adequate cure, on the other hand, the N/H_3PO_4 ratio is reduced only slightly in the course of the leaching treatment. In these cases, where the residual N/H_3PO_4 ratio remains above 1, the fabrics retain their flame-resistant properties even though the add-on is appreciably lower. These data clearly indicate that the permanence attained is practically unrelated to the phosphate content once the minimum requirement of 6-7% has been satisfied.

Uniformity of Treatment. It has been postulated in the past that the added phosphate tends to concentrate preferentially in the yarns of lower twist. This would lead to a preponderance of phosphate in the filling threads. In an attempt to substantiate or repudiate these claims, a series of treated fabrics were tested as to the phosphate content of the warp and fill threads. The analytical data of Table 13 indicate that no such preferential fixation occurs, the phosphate being uniformly distributed throughout the fabric. In some cases the use of heavily sized fabrics did make it difficult to obtain a uniform distribution of the flameproofing mixture. This, too, would tend to produce a higher phosphate concentration in the filling threads since the warp is generally more heavily sized. This could not be completely obviated even by the use of effective wetting agents. It is preferable, therefore, with this type of flameproofing treatment, which is so greatly dependent upon adequate penetration of the fabric, to use cloth which has been rendered highly absorbent by a preliminary desizing treatment.

Optimum Curing Conditions. In an attempt to fix the variables of the curing process in the urea-diammonium phosphate flameproofing system, an extended series of experiments were conducted in which a great

Table 13. Distribution of Phosphate in the Warp and Filling Threads of Treated Fabric*

Cure Time min.	Weight Ratio warp/filling	% H_3PO_4		H_3PO_4 Ratio warp/fill (by weight)	H_3PO_4 Ratio warp/fill (by area)
2	1.42	3.6	3.3	1.09	1.55
	1.32	3.4	2.6	1.30	1.72
3	1.28	7.5	8.2	0.92	1.17
	1.28	7.1	6.8	1.04	1.33
4	1.34	7.7	7.5	1.02	1.37
	1.38	8.4	7.7	1.09	1.50
5	1.35	8.8	8.6	1.02	1.38
	1.38	9.4	5.7	1.65	2.28
6	1.46	9.5	8.8	1.07	1.57
	1.37	9.5	9.3	1.02	1.40
7	1.31	8.7	8.5	1.02	1.34
	1.28	8.7	8.4	1.03	1.32
8	1.36	10.0	7.8	1.28	1.74
	1.29	10.0	8.6	1.16	1.50
9	1.33	10.0	8.9	1.12	1.49
	1.35	9.7	8.1	1.20	1.62
10	1.31	10.8	10.1	1.07	1.40
	1.40	10.3	9.5	1.10	1.52

* Regular 8.5 oz. herringbone twill treated with a 46% solution of urea: diammonium phosphate (4.4 : 1 molar) containing 0.15% turkey red oil; cured at 180° C. and leached for 30 minutes in cold water.

many specimens of herringbone twill were cured at various temperatures for different lengths of time and studies made of the resistance of the fabric to sea water leaching and laundering and the tensile strength of the treated fabric. The number of specimens employed for any one set of curing conditions varied from 5 to 30, depending upon the consistency of the results obtained. In essence, the treating process consisted of immersing in a 46% solution containing urea and diammonium phosphate in the ratio of 2 to 1 by weight, or 4.4 to 1 molar. The fabric was then squeezed to a wet pickup of approximately 100%, air-dried, cured, washed in hot and cold water and finally air-dried. The effect of cure time and temperature upon the resistance of the treated fabric to the sea water leaching test is summarized in Table 14. It was possible as a result of these investigations to determine the minimum times of cure required at each curing temperature. In Table 15 a similar set of data are presented for the resistance of the treated fabric to laundering in 0.5% G.I. soap. Comparison of the two series will indicate that the sea water leaching test is a more severe criterion of the permanence of the treatment than six laun-

Table 14. Effect of Cure Time and Cure Temperature Upon the Resistance of UDAP Fabric to a 2-Hr. Leach in Sea Water
(45°-Microburner Test)

Cure Temp. °C.	Cure Time min.	Add-On %	Afterflame sec.	Afterglow sec.	Char Area in ²
150	10	—	39	0	B.E. **
	15	—	17	0	3.2
	16	17.0	0	0	3.2
	18	16.9	19	0	3.5
	20	16.7	0	0	2.8
	22	13.9*	19	0	3.5
	24	13.7*	44	0	B.E.
	25	15.9	0	0	2.6
160	11	16.7	19	0	3.3
	13	16.7	0	0	3.0
	15	15.5	0	0	3.2
	20	16.1	0	0	3.2
	25	15.9	0	0	3.0
170	8	16.7	0	0	3.1
	10	16.6	0	0	2.7
	12	16.2	0	0	2.8
	15	—	0	0	2.4
180	4	12.7	42	0	B.E.
	6	16.7	14	0	3.1
	8	15.6	23	0	3.3
	10	16.6	14	0	3.2
	12	16.4	0	0	2.5
	15	15.8	0	0	2.8
190	4	16.1	15	0	3.4
	6	17.3	0	0	2.7
	8	16.9	0	0	2.7
	10	16.4	0	0	2.5
	12	15.1	0	0	2.9
200	1	1.5	53	60	B.E.
	2	3.4	46	0	B.E.
	3	15.6	1	0	2.6
	4	14.0	43	0	B.E.
	5	17.0	0	0	3.0
	6	15.7	0	0	3.0

* Insufficient add-on for permanent flameproofing.

** B.E.—Burned to the end.

derings in G.I. soap. In either case it is apparent that the permanence of the treatment shows the customary improvement with an increase in either the time or temperature of cure. The corresponding variation in the residual strength of the fabric is shown in Table 16. As previously indicated, working at odds with the permanence obtained, the strength is progres-

Table 15. Effect of Cure Time and Cure Temperature Upon the Resistance of UDAP Fabric to Laundering in G.I. Soap
(45°-Microburner Test)

Cure Temp. ° C.	Cure Time min.	No. of Launderings	Afterflame sec.	Afterglow sec.	Char Area in ²
140	20	1	0	0	2.4
		3	0	0	2.3
		6	44	0	B.E.*
	30	1	0	0	2.4
		3	0	0	2.3
		6	41	0	B.E.
	40	1	0	0	2.5
		3	0	0	2.4
		6	0	0	2.1
160	15	1	0	2	2.7
		3	0	0	2.9
		6	0	0	2.6
	20	1	0	0	2.6
		3	0	0	2.8
		6	0	0	2.6
	25	1	0	0	2.6
		3	0	0	3.0
		6	0	0	2.5
180	10	1	0	2	2.6
		3	0	0	2.3
		6	0	2	2.1
	12	1	0	0	2.6
		3	0	0	2.5
		6	0	2	2.3
	14	1	0	2	2.6
		3	0	0	2.6
		6	0	2	2.2
190	4	1	0	0	2.5
		3	0	0	2.4
		6	0	0	1.9
	6	1	0	2	2.7
		3	0	0	2.3
		6	0	2	2.1
	8	1	0	0	2.6
		3	0	0	2.3
		6	0	3	2.1
200	4	1	0	0	2.6
		3	0	2	2.3
		6	0	4	1.9
	5	1	0	2	2.7
		3	0	2	2.2
		6	0	3	2.1
	6	1	0	0	2.7
		3	0	2	2.3
		6	0	3	1.9

* B.E.—Burned to the end.

Table 16. Variation of Fabric Strength with Time and Temperature of Cure.
(1-inch Raveled Strip Test)

Cure Temp. °C.	Cure Time min.	Warp Tensile Strength * lbs./in.
Untreated 8.5 oz. Herringbone Twill		
140	20	131
	30	83
	40	78
150	40	77
	10	75
	15	70
	16	72
	18	73
	20	74
	22	74
160	24	75
	11	73
	13	70
	15	71
	20	67
170	25	64
	8	69
	10	66
180	12	65
	4	85
	6	69
	8	63
	10	61
	12	58
190	14	54
	4	71
	6	67
	8	55
	10	50
200	12	50
	1	100
	2	82
	3	74
	4	66
	5	59
	6	50

* Average of ten specimens.

sively degraded by increasing the intensity or duration of the curing period, though the majority of the loss occurs in the first few minutes of curing in all cases.

It is obvious that in order to obtain the best possible fabric by this process, it is necessary to compromise the permanence with the loss of

strength suffered. Setting the resistance to 2 hours' immersion in sea water as the primary requirement, the optimum conditions for the treatment are represented diagrammatically in Figure 5. Since it is also desirable to retain the maximum amount of fabric strength and, at the same time, keep the curing time sufficiently short to be commercially practical, the preferable curing conditions for this treatment were selected as 13 minutes' cure at 160° C.

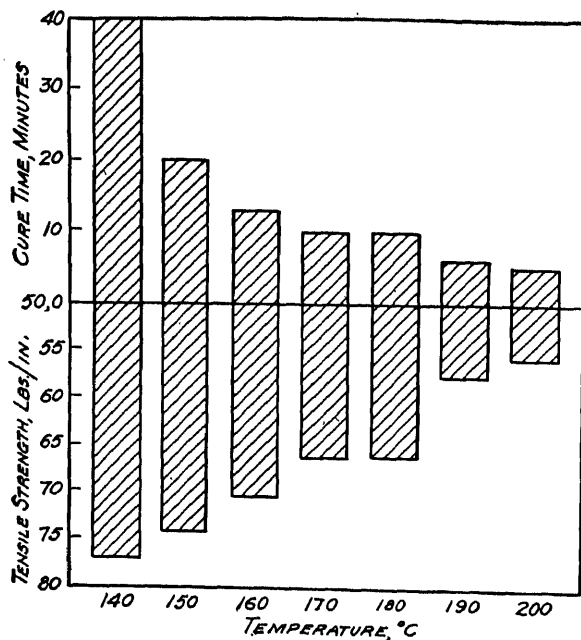


Figure 5. Optimum curing conditions for the UDAP Process.

In order to compare the performance of a flameproofed fabric treated according to the above process with that of the other available durably treated fabrics, a small-scale mill run was carried out. The exact conditions specified could not be attained on the available equipment, but the process was essentially as follows:

Impregnating Bath

Urea	300 lbs.
Diammonium phosphate	150 lbs.
Tergitol	1 lb.
Water	339 lbs. (41 gals.)
Total volume	80 gals.
Concentration	56%
Approximate pH	8.0

The squeeze rolls were adjusted for an 80% wet pickup, producing a wet add-on of 45% from the 56% solution. This is comparable to the desired 100% pickup from a 46% solution. The cure was carried out for 7 minutes, 10 seconds at 174.4° C., which was somewhat less than the optimum combination desired. The treated fabric was finally washed in hot and cold water, dried and subjected to standard finishing processes.

Comparisons of this treated fabric with several other durably flameproofed materials are described in the following chapter, with respect to the performance characteristics of the fabric itself as well as the physical and physiological influences which might be exerted upon the wearer of a flameproofed garment. Identical evaluation data are also presented for a commercially developed fabric processed with a similar but perhaps more complex flameproofing mixture.

The variables existent and problems encountered in the commercial application of this type of flameproofing treatment are considered in the following section.

c. Industrial Processing

William P. Hall

Extensive development has been carried out on the commercial application of the modified cellulose method of imparting flame-resistance* and substantial quantities of commercially treated materials have been produced.

As far as textiles are concerned the processes developed may be applied with equal success to loose fibers, yarns or fabrics. This discussion, however, will deal only with the commercial application to cotton fabrics, although the processes may also be applied to cellulose rayon and protein fabrics.

(1) *Fabric Preparation*

Since this method of flameproofing involves a reaction with the cellulose it is beneficial to have the fabric in the pure form, that is, sizing and natural waxes and other impurities should be removed. This is usually accomplished by desizing with enzymes and scouring with detergents and caustic soda followed by washing and bleaching. The reactivity of the flame-retardant chemicals toward the cellulose may be further increased by mercerizing the fabric completely. This treatment primarily increases the durability of the finish to washing and leaching.

* Various aspects of the developments described are covered by patent applications of Joseph Bancroft and Sons Co., Wilmington, Del.

In case the fabric is to be dyed or printed it is desirable to apply such processes prior to the application of the flameproofing treatment. This is recommended for several reasons: first, to obtain uniform dyeings it is essential to distribute the dyestuff uniformly upon the fibers, and this is not possible after the finish has been applied; second, the application of dyestuffs of good durability such as vats, naphthols, and pigments involves the use of strong chemical solutions having a detrimental effect upon the flame-resistant finish.

It is therefore evident that printing and dyeing should be done prior to flameproofing and should preferably involve the use of vat and naphthol dyes to obtain maximum color durability. The application of the finish may produce a slight change in shade, this change being dependent primarily upon the type of dyestuff used. In general, however, the change is insignificant and a suitable range of shades may be obtained without difficulty. The use of mineral dyeings is possible but not recommended since the deposition of large quantities of metallic oxides and salts in the fabric may produce an undesirable "afterglow" condition.

The dyeing with pigment mixtures containing plastic and resinous binders is possible but not recommended, especially if the pigments are of a mineral character in which case an "afterglow" condition may be produced in the finished fabric. Besides, the binders used, if they are combustible in nature, may undesirably interfere with the flame-retardant properties.

A pure mercerized dyed fabric of good absorbency gives the best all-around results. Pretreatment with sizing materials may be practiced provided such materials do not detrimentally interfere with the successful applications of the process. If protein or carbohydrate sizing materials are used the flame-retardant chemicals will react with these materials as well as with the cellulose of the fabric. However, the use of large quantities of such presizing materials is not desirable since the stiffness and absorbency of the fabric will be undesirably altered.

(2) *Preparation of Flameproofing Solution*

As shown in the two preceding sections of this chapter, the composition of the flameproofing mixture may be varied by altering the chemical ingredients or by altering the method of preparing the mixture.

The main ingredients may be divided into two classes, namely, the acids and the nitrogen compounds. These may vary as previously shown between wide limits, but each is essential to the successful application of the process.

For the same ingredients different results may be obtained by varying the method of preparing the mixture. For example, one or several of the ingredients may be fused at high temperatures and then added to the

mixture, or the ingredients may be divided into different sections and these reacted together followed by a mixing of the different sections to produce the final impregnating mixture.

Acids of phosphorus, such as orthophosphoric and pyrophosphoric, are usually employed as well as the more complex amido phosphoric and phosphonitride acids. Many nitrogen compounds, principally those containing a high percentage of nitrogen such as urea, guanidine, dicyandiamide, melamine and biuret, also find wide use.

A suitable mixture may be prepared by mixing in the cold 1000 lbs. diammonium phosphate, 2000 lbs. urea and 3000 lbs. water. Another mixture is prepared by mixing together 215 lbs. orthophosphoric acid (75%), 3000 lbs. urea, 160 lbs. guanidine carbonate and enough water to make 100 gallons. Another mixture is prepared by reacting together at high temperatures 200 lbs. of orthophosphoric acid (75%) and 400 lbs. of urea; after cooling the following are added: 28 lbs. mill ammonia, 108 lbs. formaldehyde (37%), and enough water to make 100 gallons.

Other auxiliary ingredients may be added to the mixture such as penetrating agents, waterproofing agents, softeners and the like. In general, the use of these materials in the mixture is not recommended.

The mixing equipment used in preparing the flameproofing mixture consists of a stainless steel tank, hooded to remove fumes, and equipped with a slow speed agitator and with suitable means of heating and cooling. The heating may be done by steam, electricity or gas and the cooling with cold brine or water. A jacketed steel tank using steam and cold water for heating and cooling is generally satisfactory. Also in the case where very rapid cooling is desired, water will not be satisfactory and super-cooled brine should be employed.

To measure and control the temperature of the mix, a thermometer or similar instrument should be inserted in the lower portion of the tank. Also, since the quantity of mixture prepared in commercial practice is usually determined by the final volume rather than weight, it is desirable to install a float type volume indicator so that the volume can be easily measured.

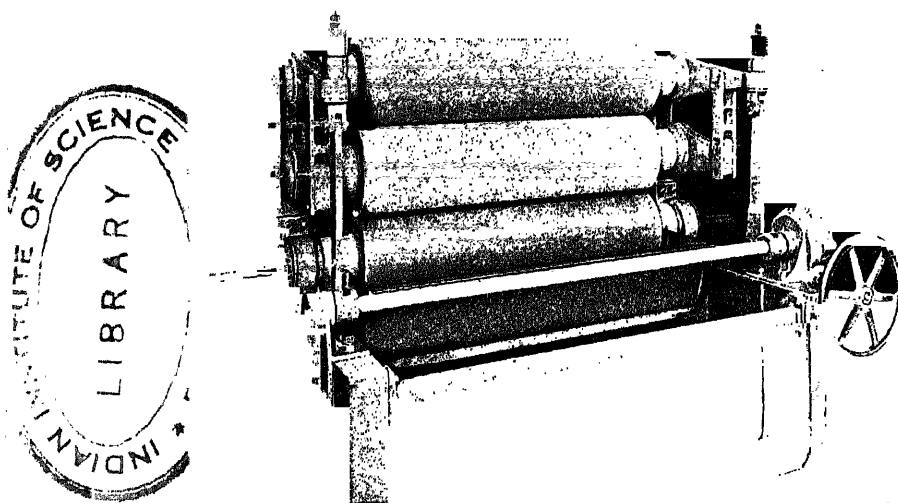
Two mixing tanks should be available to insure a steady supply of solution, or one mixing tank and one jacketed or insulated storage tank may be used. The storage tanks or mixing tanks should feed directly to the solution application equipment, the steel or iron feed pipes being insulated to prevent excessive cooling of the mixture in passing from the tanks to the impregnating bath (see Figure 10).

Since the flameproofing of fabrics involves the use of concentrated chemical solutions the quantity of chemicals used becomes very large as compared with other textile processes. It is therefore necessary to insure sufficient storage space and the necessary mechanical equipment for the handling of such large quantities of chemicals. For example, processing

10,000 yards of fabric weighing 8 oz./yd. may require 1700 lbs. of ammonium phosphate and 2400 lbs. of urea.

(3) Treating Process

The flameproofing solution may be applied by any of the methods well known in the textile industry. However, the most common procedure is to impregnate the fabric with the solution and remove the excess by squeezing. This procedure is referred to as "mangling" or "padding" and the equipment as a mangle or padder. A two-roll mangle containing a jacketed stainless steel box with sufficient dips to insure a thorough impregnation of the fabric generally serves very well, but a three-roll double dip mangle with a jacketed stainless steel dip box is recommended since this method of application insures a uniform and efficient penetration of the fabric.



Courtesy of H. W. Butterworth & Sons Company, Philadelphia, Pa.

Figure 6. Three-roll micro-set mangle.

The jacket on the bath should be steam or hot water heated to insure temperature control of the solution which in most cases, due to the high solid content, is applied at elevated temperature to prevent undesirable crystallization at lower temperatures. To control the temperature a thermometer or similar instrument should be inserted in a suitable place in the bath. The type of squeeze roll used in the mangle may be of steel, wood, husk or rubber. Brass is not recommended due to the presence of ammonia in some of the flameproofing solutions. For the same reason brass rollers should not be used in the bath.

The squeezing mechanism should be capable of applying a uniform squeeze from selvage to selvage at both high and low pressures. Mangles where the pressure is applied by weights or hand set screws are satisfactory but a pneumatic pressure mangle with individual cylinder pressure adjustment is highly recommended since the uniformity can be easily controlled and duplicated from run to run.

The wet pickup and the solution concentration determine the quantity of chemicals deposited on the fabric. For a particular solution the squeeze on the cloth is therefore adjusted to obtain the desired quantity of chemicals on the fabric. By wet pickup is meant the difference in weight between the fabric before and after impregnation. For most applications 75% to 100% pickup is satisfactory.

After applying the solution, the cloth may be dried directly or it may be left in the moist condition for a short time. To increase speed of production and decrease labor cost the impregnating mangle is usually placed in front of the drying unit and the cloth passes directly from the impregnation to the drying without being folded or batched.

(4) *Drying*

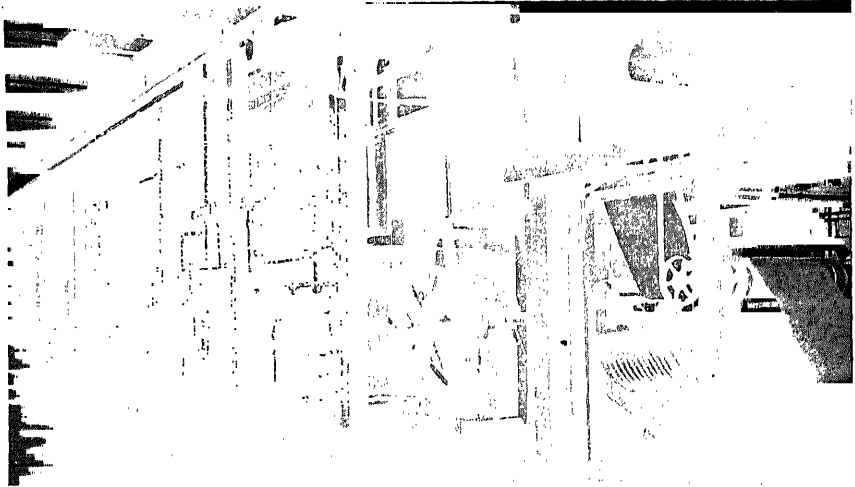
Since the quantity of solid material deposited on the cloth is usually high, the quantity of water to be removed is not excessive. It usually averages about 50% of the solution deposited. Such drying equipment as hot cans, flue dryers, air-lay dryers, frame dryers, or loop dryers may be used successfully. The most satisfactory method of drying is obtained with a tenter frame where the cloth is held by clips and tightly stretched while drying, thus affording control of the width of the cloth. This width control is sometimes very important and cannot be obtained with the other types of drying equipment. Due to the stiffness of the dried fabric, especially the heavy variety, the loop and air-lay type of equipment is the least recommendable since the formation of loops and folds at this stage of the process may permanently injure the cloth.

Since the cloth usually carries a heavy quantity of chemicals it is advantageous while the moisture content is still high to prevent the cloth from passing over stationary objects such as bars or rails as the flame-retardant mixture will be scraped off, resulting in an unnecessary loss of chemicals. This may be prevented by passing the cloth over freely rotating rollers, or passing it through a preliminary flue dryer where the excess moisture may be removed quickly while the cloth is freely suspended. Infrared heating equipment such as infrared lamps may also be used for this purpose.

The cloth is usually quite hot and shows an acid reaction on the completion of the drying operation. This is quite an undesirable state and to prevent excessive detrimental action to the fabric it is usually passed

directly through a cooling chamber or over cooling cans before being batched into rolls (see Figure 10).

The cloth after drying and cooling is quite stiff and care should be taken to prevent the formation of creases and folds as this may permanently injure the fabric. It is therefore evident that the cloth should always be



Courtesy of Joseph Bancroft & Sons Company, Wilmington, Del.

Figure 7. Commercial impregnation and drying installation showing a continuous range consisting of a mangle, overhead flue dryer and tenter frame.

wound into rolls after drying rather than folded into boxes as is often the practice in regular textile processing.

(5) *Curing*

The curing or aging of the impregnated and dried fabric represents one of the most important steps in the process. As previously described, it is during the curing that the combination between the cellulose of the fabric and the acid phosphates of the solution takes place. In many cases additional changes also take place in the chemical ingredients themselves during this curing operation.

The curing is controlled by varying the time and temperature and is determined primarily by the composition of the impregnating mixture, type of fabric and the degree of durability desired. Excessive time of curing or very high temperatures cause undesirable changes in the physical properties of the fabric, especially in the tensile and tearing strength, although under such conditions the durability of the finish is substantially increased. It is therefore necessary to determine and control carefully the curing conditions for a particular run in order to obtain the most satisfactory all-around results.

For all practical purposes a temperature range of from 300° F. to 350° F. is satisfactory with the time varying from 15 minutes to 3 minutes. As an average, using medium and heavy weight cotton fabrics, a time of 7 minutes and a temperature of 335° F. give good results.

The temperature range of curing is obtainable with standard textile drying and curing equipment but the time of curing is excessively long for regular equipment. A loop or air-lay type of dryer would be satisfactory as far as time and temperature are concerned but these machines are not well adapted to this part of the process as will be presently shown.

Ordinary type drying and curing equipment not of the loop and slack



Courtesy of Andrews and Goodrich, Inc., Boston, Mass.

Figure 8. Gas-heated curing oven.

type such as drying frames, super-heated drying cans, flue dryers, and resin curing chambers may be used with success. However, the output of these machines would be small using material which required a 7-minute cure time. The construction of super-heated cans of sufficient number or a frame of sufficient length to insure proper curing and a satisfactory output would be impractical and uneconomical. This leaves the flue type dryer or curing chamber as the only suitable equipment which will produce the proper conditions of time and temperature and at the same time assure a satisfactory practical commercial output.

Generally, this type of equipment consists of one small preheating

chamber followed by a larger baking chamber. The cloth is carried in open width over a series of rollers while hot air is being circulated around the cloth. In the preheating section the heated air is blown through slots directly onto the cloth in order to bring it quickly to the desired temperature, while in the baking section the cloth is maintained at this temperature for the desired length of time.

To maintain the temperature in the curing chamber at the desired value, the air is circulated by fans through an indirect heat exchange unit where the heat may be supplied by steam, gas or oil. The direct heating of the circulating air by gas or oil burners is also practiced. The curing of the fabric by infrared lamps or by electronic means is not practical and is uneconomical.

The cloth while in the ager is kept in open width and passes under tension over a series of rollers at the top and bottom of the curing chamber; this prevents the formation of sharp creases which would seriously and permanently injure the fabric. The necessity of keeping the fabric from folding and creasing makes the use of loop and air-lay type of curing equipment unsuitable except for very light fabrics where the stiffness and weight would be small.

The size of the curing equipment, that is, the length of cloth in the machine at one time, together with the length of curing time determines the production capacity of a given piece of equipment. For a given curing time of 6 minutes, for example, and with 120 yards of cloth capacity a production rate of 20 yards a minute may be obtained.

The cloth is slightly acidic upon completion of curing and it is best that the fabric be cooled before being batched into rolls. This procedure will prevent any unnecessary degradation in case it is necessary to store the cloth for a substantial length of time before washing.

(6) *Washing and Drying*

The cloth after curing contains a large quantity of soluble material which it is desirable to remove in order to reduce the stiffness and return the fabric more nearly to its original hand and feel. To avoid the formation of creases at this stage it is recommended that open width washing equipment be employed such as jigs, open width soapers and vertical or horizontal multiroll washers.

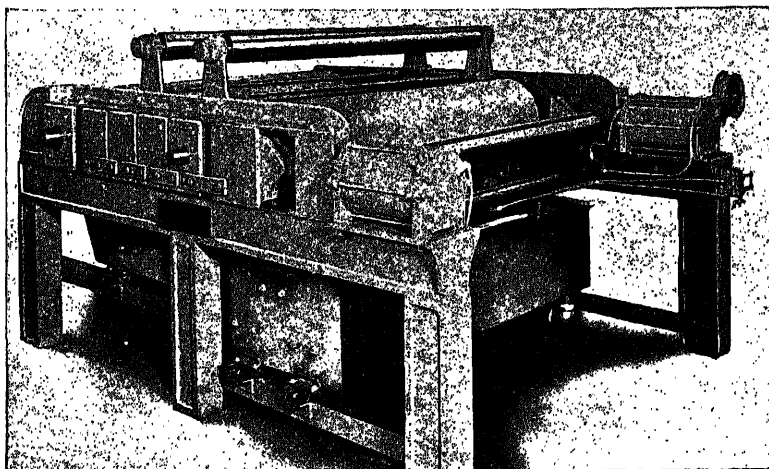
In jig washing operations the cloth is passed back and forth under tension through a water bath until the soluble chemicals are removed and is finally squeezed or extracted to remove the excess water.

In the open width soaper the cloth passes under tension through a series of multi-dip wash boxes containing hot water, the excess water being removed by squeezing after each box. Any number of wash boxes may be employed but two to four boxes are sufficient for most fabrics.

In the vertical or horizontal multiroll washers the cloth passes through

a series of squeeze rollers while clean hot water is being sprayed on the cloth just prior to each squeezing operation.

It is advantageous to use hot water (180-190° F.) for the washing as it facilitates the removal of the soluble uncombined materials. A small quan-



Courtesy of H. W. Butterworth & Sons Company, Philadelphia, Pa.

Figure 9. Six-roll horizontal washer.

tity of detergent may be employed but it is not necessary as a very satisfactory wash can be obtained by the use of ordinary hot water.

After washing and removal of the excess water the cloth may be dried by any type of drying equipment previously discussed including the loop and air-lay type dryers. The use of a drying frame is, however, recommended as the width of the cloth may be controlled in this type of equipment. To save labor cost and speed production the washing and drying may be combined into one operation by placing the washing equipment directly in front of the drying unit and passing the cloth from the washer to the dryer without interruption.

The flame-resistant fabric may be used as is or it may be given further auxiliary processing such as softening, waterproofing, plastic coating, calendering or sanforizing.

2. DOUBLE-BATH PRECIPITATION TYPE

a. Fundamentals of Processes

S. Coppick

Although considerable protection is afforded by the use of certain soluble salts, the very temporary nature of the imparted fireproofing characteristics limits their use in clothing fabrics. The most obvious means for greater permanence lies in the application of insoluble salts. However,

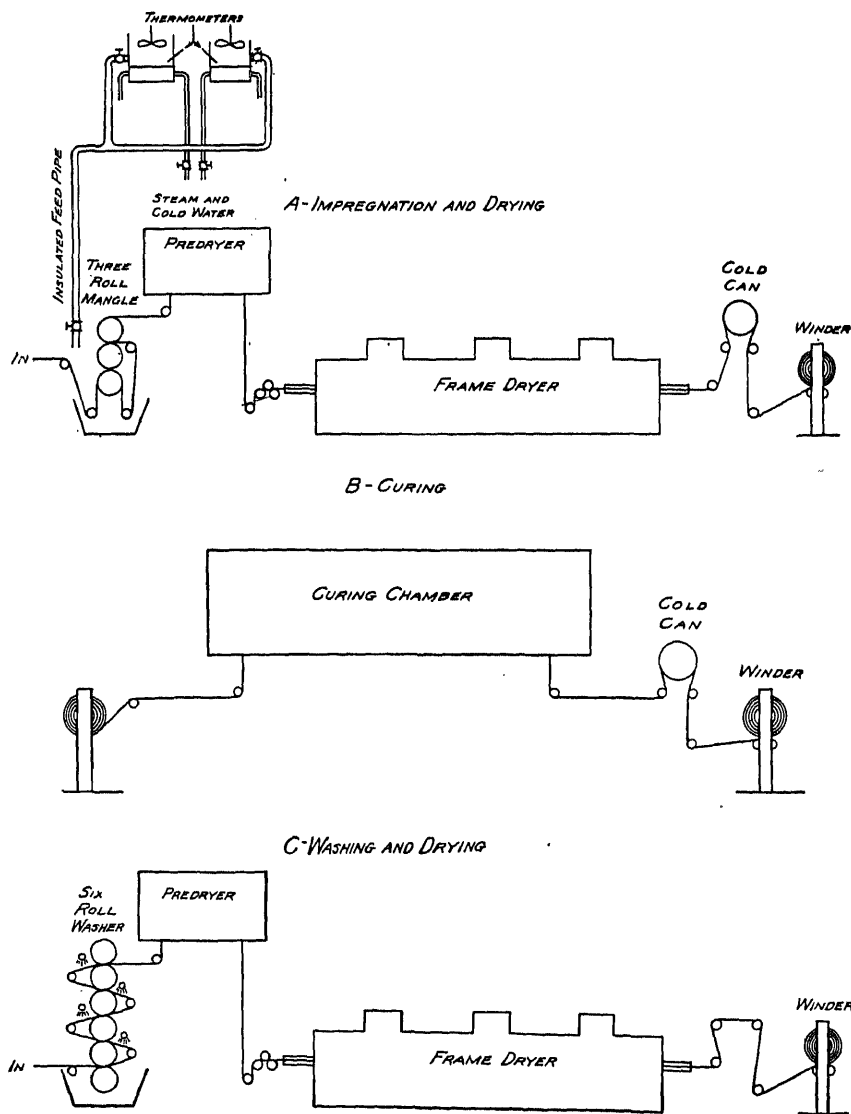


Figure 10. Commercial installation for the processing of fabrics by the urea-phosphate type of treatment.

aside from the technical difficulties, certain fundamental considerations arise here which greatly reduce the number of possible compounds having fire-retarding properties. As has been pointed out in the earlier theoretical sections, the simple salts which impart the desired thermal properties to cellulose embrace those which are capable of easy decomposition at flame temperatures to produce either a strong alkali or a strong acid, and these products are directly responsible for the retardant action. The molecular

instability of the salts of weak acid and strong base or of weak base and strong acid fortunately affords numerous compounds which will undergo the desired thermal decompositions. However, the needed quality of insolubility is generally directly adverse to this thermal instability, the bonding energies which resist ionization and solution also favoring retention of the original molecular state at elevated temperatures. Thus we have the effective action of the soluble ammonium phosphate and the non-retardancy imparted by the calcium salt. Similar radical divergence is exhibited in the effects of ammonium, calcium and barium sulfate and of sodium, calcium and barium carbonate or borate. It is at once apparent that retardancy will be extremely limited for the simple insoluble salts and will be confined to compromises in the field of the amphoteric anions and cations, for instance the phosphates and borates of tin, zinc, aluminum and magnesium, as well as the stannates, tungstates, aluminates, etc.

The greatest possibilities for insolubility combined with efficient fire-retarding qualities lie in the non-salt type, namely the easily reducible hydroxide or hydrated oxides of the metals whose catalytic influence is assumed to direct the course of cellulosic thermal decomposition as previously shown in Chapter III. These include stannic, plumbic, ferric, titanic and chromic oxides as well as those of zinc, cerium, bismuth, tungsten, arsenic and silicon.

Application of both types of these insolubles to cellulose is best carried out by metathetical reactions within the cell wall and lumen of the fiber and in the case of woven fabrics at the fiber to fiber interface in the component yarns and in the interstices between the yarns themselves. Such methods provide for better distribution and location of the retardant as well as serving to support better permanence than the more direct process of attempting to pad these materials into the fabric. It appears also, as will be discussed more fully later, that a more active ingredient may be obtained by precipitations in the cellulose membrane structure.

Characteristics of Processes. The reactions are carried out usually via a multi-bath process wherein the fabric is immersed in a solution of a soluble salt containing the desired ion or complex and then dried. The second medium contains the coagulant, which functions either to supply the ionic component required for precipitation, to change the pH, or serve as an oxidant. This latter medium may be either a liquid, vapor or gas, but in the usual case consists of an aqueous solution. The fabric is finally washed, further finishes applied, and dried. The simplest functional process involves a dual impregnation with intermediate drying which leads to the general designation of "Double Bath," although practical applications are sometimes considerably more complicated, multi-components being applied in successive stages.

From the early development of the process by Perkin,¹⁸ numerous for-

¹⁸ Perkin, W. H., U. S. Patent 844,042 (Feb. 12, 1907).

mulations have been proposed and practically all of the known insoluble inorganic compounds have been suggested for retardant purposes. The very nature of the process leads to considerable confusion since the application is indirect and in the majority of cases little if anything is known concerning the actual chemical composition of the material which is precipitated in the fabric from the complex systems used. It is prevalently assumed that such compounds as stannic tungstate, zinc stannate, etc., are the chemical identities affixed to the fiber but from the variable conditions of the precipitations it is much more probable that what is actually obtained consists of complex and variable mixtures of the oxides, hydroxides, and acids of the component metals. Furthermore since many of these amphoteric materials are known to exist as isomorphous mixed crystalline structures in a wide and continuous variety of stoichiometric ratios, even on fundamental grounds they are best considered as their component oxides, particularly in the case of the complex multi-bath formulations. At flame temperatures this is certainly the case.

In systematic studies of the relative efficiencies of a number of insoluble retardants compared with the well-known solubles, Ramsbottom and Snoad¹ came to the conclusion that the multi-bath process is relatively ineffective and state that it is probable that the apparent resulting fireproofed fabric is due largely to the soluble salts absorbed on the precipitated particles and incompletely removed by washing. The add-on requirements for this process are found to be particularly high in most cases compared with the effective but soluble borax-boric acid mixture (Table 17).

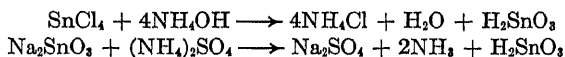
Table 17. Relative Efficiencies of Various Insoluble Materials Compared With the Soluble Borate Mixture
(*Ramsbottom and Snoad*¹)

	Add-On *
	%
Borax-Boric Acid 1 : 1	10
Ferric hydroxide	25
Antimony oxychloride	30
Stannic oxide, hydrated	40
Titanic hydroxide	40
Bismuth trioxide, hydrated	40
Zinc stannate	40
Aluminum borate	59
Lead peroxide	60
Cerium hydroxide	69
Aluminum hydroxide	70
Chromic hydroxide	91
Silica, hydrated	100
Aluminum silicate	100
Magnesium silicate	116
Magnesium ammonium phosphate	125

* Minimum quantity necessary to prevent flame propagation.

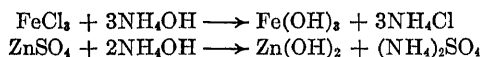
Impregnation Reactions. The chemistry of the application of the insoluble materials most commonly entering into flameproofing formulations is as follows:

1. The precipitation of stannic acid, *i.e.*, hydrated stannic oxide, is usually carried out by variations of either of two general reactions which involve the alkaline hydrolysis of a stannic salt or the acidification of an alkaline stannate:

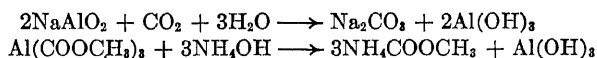


Similar neutralization of stannates with ammonium, zinc or aluminum acetate or even acetic acid are also conveniently used.

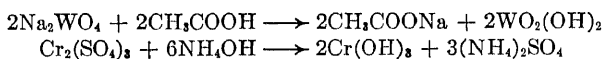
2. For impregnations with ferric hydroxide, the alkaline hydrolysis of the chloride, sulfate or acetate suffices, as also with zinc:



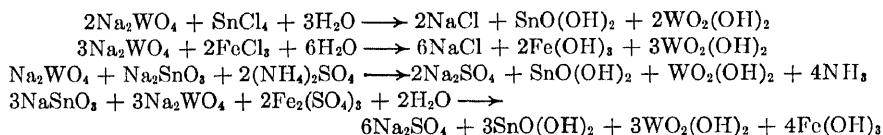
3. With alumina, precipitation involves either the acidification of an aluminate or the hydrolysis of the acetate:



4. In the case of impregnations with tungstic acid, the sodium salt is usually acidified, while chromic hydroxide is brought down from its sulfate by the addition of ammonia:



5. Complex systems involving two or more of these reactions are prevalent in the literature, and the products are best considered as the mixed hydroxides rather than such compounds as stannic or ferric tungstate:



It is of course obvious that the stoichiometric relations set down by the above equations are the ideal and are dependent primarily upon constant pH relationships which are seldom if ever met with in double-bath precipitations. The actual composition of the hydroxyl compounds laid down in a fabric will depend upon the concentrations and pH at the point location where precipitation takes place. This in turn will depend on the external concentration of the in-filtering second bath and the solution and diffusion rates of that material laid down by the first bath within the fiber.

It is then apparent that the number of individual phases, the composition of these phases and their relative amounts are greatly dependent upon the variables in the process which include concentrations, temperature and time, as well as the presence or absence of pH controlling media such as added acid or base to the second bath. Each of the precipitated phases has a different solution tendency directly proportional to the final pH of the fabric before the washing procedure, so that the reversal of the impregnation proceeds, and the final result is an equilibrium which may be varied widely by suitably setting the conditions of the treatment.

Recent Developments. A simplification of the double bath procedure has been advanced by Hopkinson,¹⁹ wherein the primary constituents capable of forming the water-insoluble precipitate are added together to the fabric in an organic solvent. Apparently this solvent should be of sufficient hydrophilic nature to enable wetting of the cellulose and penetration of the constituents, but should have a low enough dielectric constant to prevent precipitation and hold the initial salts in solution molecularly. Such properties appear to be satisfied by both ethylene and diethylene glycol mono-ethyl ether, glycerin, acetamide, triethanol amine and tricresyl phosphate. The insoluble salts of zinc, aluminum, manganese and magnesium may be precipitated in the fiber as the borates, phosphates, tungstates, etc., by first treating the fabric with an organic solution containing the desired ions, drying and finally subjecting the material to water.

This process avoids the difficulties usually encountered in double-bath methods wherein variable precipitating conditions result from changes in concentrations, pH, solubilities and diffusion rates occurring during the second bath impregnation. In the organic solvent treatment the active ingredients are deposited uniformly throughout the fabric and are in intimate contact. The whole of the water-insolubilizing process depends solely upon the inward rate of water penetration in the second bath. A typical example of the method involves the impregnation with a solution of zinc chloride and borax in a glycol solution followed by a water wash to precipitate zinc borate. The use of the organic solvent has the added advantage of permitting the additions of binding resins directly to the first bath.

Precipitation Conditions. In extensive experiments performed by the Department of Agriculture,²⁰ the precipitation conditions appear to be critical factors in determining the flame resistance of treated fabrics. For instance when sodium stannate is precipitated with sulfuric acid rather than with ammonium sulfate as in the Perkin process,¹⁸ a deposit of

¹⁹ Hopkinson, H., U. S. Patent 2,250,483 (July 29, 1941); U. S. Patent 2,343,186 (Feb. 29, 1944).

²⁰ Leatherman, M., U. S. Dept. of Agriculture, Circular No. 466 (March, 1938).

greater flame-reducing capacity is obtained. Similar improvement is obtained via precipitations carried out with metallic sulfates such as those of copper, chromium, manganese and iron. In these latter treatments an undetermined amount of the metallic hydroxides other than tin remains in the fabric. The mechanism forwarded for the advantage of acid rather than weak base precipitants is that the latter is strongly absorbed on the highly colloidal deposit and poisons its catalytic directionalization of cellulosic dehydration at elevated temperatures.²⁰

The use of stannic oxide alone appears to have further disadvantages as pointed out by the British Air Ministry.¹ Fabrics thus treated are extremely sensitive to strength deteriorations in the presence of sunlight. However, in the case of the mixed oxides, this tendering is reduced to a great extent. In the experiments of Leatherman,²⁰ fabrics exposed outdoors near Washington, D. C. over the months from March to September of 1934 were rendered useless if they contained the stannic oxide alone, were degraded considerably in the presence of stannic and ferric, and remained practically unchanged by the three-component system involving chromic oxide (Table 18). The most effective preserving components are

Table 18. The Sensitivity of Fabrics to Sunlight When Impregnated With Metallic Oxides (6 months' outdoor exposure)

(Leatherman²⁰)

Treatment	Average Breaking Strength kilo.	Ash Content of Fabric Including Oxides %
None (unexposed)	39.3	1.0
None (exposed)	24.9	1.0
Stannic Oxide	2.0	7.25
Stannic Oxide + Ferric Oxide	12.8	8.37
Stannic Oxide + Chromium Oxide	16.7	6.27
Stannic Oxide + Ferric Oxide + Chromium Oxide	24.5	9.95

those producing a yellow coloration to the fabric and the mechanism is presumed to be the absorption of the active wave lengths.

Reduction of Afterglow. Normally metallic hydroxides, although producing adequate flame resistance in a fabric actually enhance its destruction by flameless combustion. The tendency towards glowing in the uncharred area is reduced by the application of chlorinated compounds, but the afterglow of charred regions is still very persistent. Recent experiments by the British²¹ show that the insoluble phosphates and borates have little or no flame-retarding properties but inhibit afterglow. Moreover, they are readily removed from the fabric by leaching processes. However, in the case of some tungstates the resistance to both flaming and glowing is fairly good, and the materials are not leached out too easily.

²¹ "Fireproofing of Textiles." Interim Report, Chem. Dept., Portsmouth (1945).

The inference is that tungstic acid functions similarly to boric and phosphoric acid to inhibit flameless combustion. Systematic studies on the incorporation of tungstic acid in double-bath precipitation involving stannic and other metallic hydroxides indicate that such is the case. In all flame-retarding systems of stannic, ferric and aluminum hydroxide, the strong glowing tendencies are reduced to either moderate or slight by the inclusion of tungstic acid, which appears to be capable of withstanding considerable water leaching. In the two-component systems involving stannic and another metallic hydroxide, the ferric seems to be the most efficient in its ability to increase the normal protection afforded by the tin alone. Moreover, only very small amounts are necessary, 1% of the iron being sufficient. These effects are shown in Table 19.

Table 19. Effect of Metallic Hydroxides and Acids on the Burning Characteristics of Fabrics

(Interim Report, Chem. Dept., Portsmouth ²¹)

Hydrated Oxide or Acid	Add-On %	Before Leaching	Burning Time (seconds) *	
			After Leaching 48 hrs. Boiling Water	% Loss During Leaching
Stannic	22.5	12	15	3
Stannic + Tungstic	21.0	0	15	5
Ferric + Stannic + Tungstic	23.0	0	0	1
Aluminum + Stannic + Tungstic	24.0	55	50	2.4

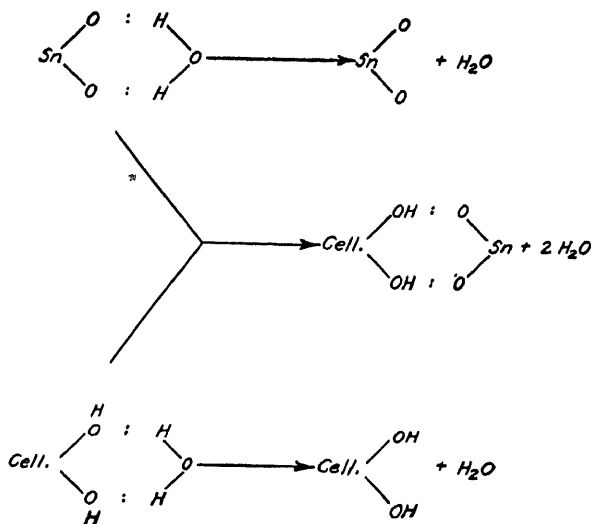
* Glowing small except for stannic alone.

General Requirements. From the above and previous considerations of Chapters II and III, it would seem that the requirements for adequate flame and glow protection in these double-bath treatments are as follows:

1. A source of a readily reducible metallic oxide or oxide mixture.
2. A source of either boric, phosphoric or tungstic acid.

The oxide may be presumed to function via the chemical mechanisms previously forwarded to prevent afterflaming, while the acid acts as the glowproofing constituent via the fundamental processes set down in the theoretical sections. However, these requirements are stipulated only for the original flameproofed fabric and do not consider the adherence and permanence of the ingredients.

Durability. It is well known that the metallic hydroxides and acids are held very tenaciously when dehydrated at cellulose surfaces and there appears to be considerable evidence for interbonding of their normal residual attractive forces with those of cellulose and water which are normally satisfied through hydrogen bridges. The three-component system may be assumed to dehydrate as follows in the regions of cellulosic disorder within as well as on the external surfaces of the fiber:



Schematic reactions for the dehydration of the three-component system: cellulose; stannic oxide; water.

The system is practically identical with the mordanting of fabrics for various dyeing processes, and may be represented roughly as in Figure 11. Here the moist cellulose and the hydrated oxide are considered as being bound to water molecules through hydrogen bonds. The structures are so

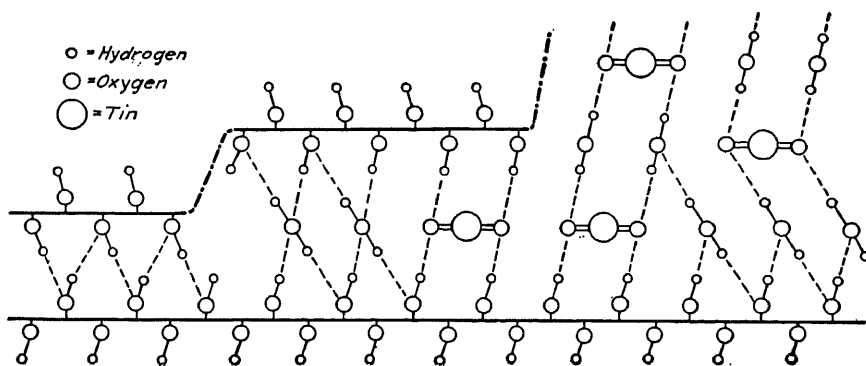
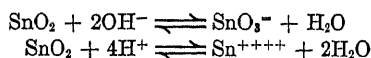


Figure 11. Schematic representation of the possibilities for hydrogen bonding of surfaces in the system cellulose-water-metallic hydroxide.

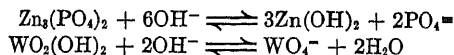
similar that surfaces may be mutually associated through the same water molecule. On dehydration of the system the free fiber hydroxyls may cellulose the oxide similar to the normal hydrate structure. The whole of the mechanism depends upon the similarity of space lattices, and the extent to which it will proceed will be determined by favorable inter-atomic distances in the oxide to permit formation of the isomorphous

surface structure. This postulation accounts for the strong adherence in the system and is very probably associated with the actual catalytic dehydration of the flameproofing action.

To further enhance permanence via a mechanical binding of the fire-retarding ingredients to the fiber, resin coatings are frequently applied. These appear to function in the dual role of preventing emulsification of the particles during laundering and to decelerate the solution and diffusion of the ingredients in detergent media. The flameproofing constituents are usually not very susceptible to minor pH changes which would tend to reverse the reaction of their formation, *i.e.*:



Thus alkali soaps and acetic acid souring normally cause only a small loss of flame retardancy. However, the anti-glow constituents appear to ionize much more readily, *i.e.*:



By virtue of this, the glow retardancy is poorly retained on laundering.

b. Laboratory Impregnations

S. Coppick

As has been pointed out in the preceding section, the active components of various double-bath formulations may be considered as a glowproofing acid and a flameproofing oxide or oxide mixture. To permit incorporation of these materials in the fabric in various combinations the simplest procedure is to immerse the material first in a solution containing one of the desired radicals, preferably the alkaline salt of the desired acid grouping. When thoroughly wetted out with the reagent the fabric samples are passed through a wringer to remove the excess liquid so that the final wet weight is about twice that of the original dry fabric. The samples are then allowed to dry at room temperature before the second steeping in a solution containing the acidic salt of the desired metallic oxide. Similar wringing and drying procedures are carried out prior to a final leaching treatment in running tap water to remove the excess soluble reagents. The third and last drying process is again conducted at room temperature, after which the fabric is conditioned and is then ready for comparative inflammability evaluation.

A preliminary survey of the relative efficiencies of a number of combinations prepared in this manner is given in Table 20. In a few cases the precipitated phases are retained by the fabric in insufficient quantities to

Table 20. Relative Efficiencies of Various Double-Bath Formulations

Active Component	Bath		Conc. %	No. 2 Reagent	Conc. %	Vertical-Bunsen		Flame Tests		Horizontal-Microburner
	No. 1 Reagent					Add-On %	Afterglow sec.	45°-Microburner Afterglow sec.	Afterglow sec.	
Glowscreening Oxide										
None	$\text{Al}_2\text{O}_3 + \text{SnO}_2$	$\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$	10	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	10	17.2	24	82	57	99
None	$\text{ZnO} + \text{SnO}_2$	$\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$	10	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	10	30.9	23	183	30	276
Sulfamic	SnO_2	$\text{NH}_4\text{OSO}_2\text{NH}_2$	20	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	20	5.2	16	109	59	216
Boric	ZnO	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	20	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	20	5.1	30	39	52	84
Phosphoric	$\text{CaO} + \text{P}_2\text{O}_5$	$\text{Na}_4\text{P}_2\text{O}_7 \cdot 12\text{H}_2\text{O}$	20	CaCl_2	20	18.4	30	110	52	312
Phosphoric	$\text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5$	$\text{Na}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$	20	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	20	7.1	23	58	115	59
Phosphoric	$\text{ZnO} + \text{P}_2\text{O}_5$	$\text{Na}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$	20	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	20	14.7	28	31	80	19
Phosphoric	$\text{SnO}_2 + \text{P}_2\text{O}_5$	$\text{Na}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$	20	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	20	32.7	29	3	65	2
Tungstic	$\text{Al}_2\text{O}_3 + \text{WO}_3$	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	10	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	10	7.1	18	86	136	63
Tungstic	$\text{Al}_2\text{O}_3 + \text{WO}_3$	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	10	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	10	24.5	22	483	48	6
Tungstic	$\text{ZnO} + \text{WO}_3$	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	10	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	10	30.9	19	191	17	206
Tungstic	$\text{SnO}_2 + \text{WO}_3$	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	20	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	20	29.4	0	29	2	33
Tungstic	$\text{SnO}_2 + \text{WO}_3$	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	20	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	20	31.3	0	19	1	33

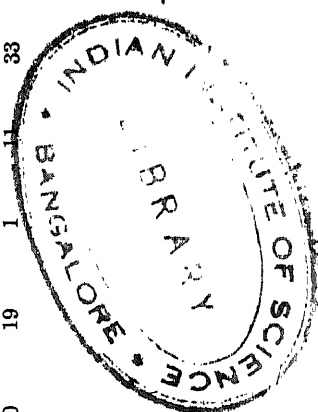


Table 21. The Effect of the Precipitation Conditions in the Stannic Oxide-Tungstic Acid System

Bath Concentration %		No. of Impregnations	Temperature Bath No. 2 °C.	Vertical-Bunsen			Flame Tests			Horizontal-Microburner		
				After- flame sec.	After- glow sec.	Char Length in.	After- flame sec.	After- glow sec.	Char Area in. ²	After- flame sec.	After- glow sec.	Char Area in. ²
No. 1 Na ₂ WO ₄ · 2H ₂ O	No. 2 SnCl ₄ · 5H ₂ O											
2.5	2.5	6	25	26	72	B.E.*	48	12	B.E.	63	5	B.E.
5.0	5.0	4	25	0	13	4.7	14	7	B.E.	29	3	5.9
10.0	10.0	2	25	0	18	4.6	0	8	3.1	7	0	3.6
20.0	20.0	1	25	0	19	4.2	1	11	3.6	33	7	5.4
10.0	10.0	2	100	25	37	B.E.	51	6	B.E.	62	4	B.E.
10.0	10.0	2	25	0	18	4.6	0	8	3.2	7	0	3.6
10.0	10.0	2	0	0	22	3.9	0	5	2.6	0	8	2.6
10.0	5.3	2	25	0	29	4.5	1	8	3.6	24	6	5.8
10.0	5.3	2	10	0	15	5.0	2	7	3.6	34	1	6.2
10.0	5.3	2	0	0	22	4.2	0	9	3.2	7	0	4.6
10.0	10.0	1	0	0	29	4.4	13	15	B.E.	47	6	B.E.
12.5	12.5	1	0	0	22	4.4	1	15	3.0	19	0	4.7
12.5	6.6	2	0	0	18	3.7	0	10	3.2	2	5	3.0
20.0	10.6	1	0	0	17	4.0	3	11	3.2	6	3	3.2

* B.E.—Burned to the end.

afford any appreciable protection, and it is only when the add-on is in the neighborhood of 25 to 30% that the combinations are truly comparable. Systems in which stannic oxide occurs as one component appear to be most efficient. In combination with phosphoric acid the glow retardancy is very good while with tungstic acid the flaming resistance is best. A compromise with good flame and fair glow resistance favors the tungstic acid-stannic oxide formulation.

Effect of Precipitation Conditions. In a more detailed study of this system it seems that the conditions under which the precipitations are carried out have considerable influence on the fire resistance of the final fabric. The procedure of employing numerous impregnations from dilute solutions is not advantageous (Table 21), and usually leads to less protection. The temperature at which the precipitation reaction proceeds also appears to influence the properties, lower temperatures favoring better protection. Table 21 also indicates that the use of a cold second bath permits a lower add-on in the final product. These conditions, however, are not too critical and either a single or double impregnation at room temperature results in products of similar retarding qualities. The most efficient afterglow protection is obtained with an excess of the tungstic acid component, thus favoring high concentrations in the first bath.

Added Glow Retardants. Further improvement in glow protection is obtained via the incorporation of the phosphoric radical in the first bath as shown in Table 22. Of the number of combinations attempted, that involving 3% sodium pyrophosphate and 8% sodium tungstate followed by 8% stannic chloride seems to be the most efficient. For adequate protection this process should be carried out twice to result in an addition of about 30% to the original weight of the fabric. However, although the treatment as applied provides the desired resistance to both flame and glow, its permanence to leaching or laundering is very poor. Prolonged immersion in tap water or even very mild washings with neutral detergents appreciably reduce the protective qualities of the fabric (Table 23). With the harsher detergents the resistance to flame and glow is almost totally lost, and it is to be noted that even slight reduction of the add-on below the original 30% causes a marked reduction of the fire resistance.

Permanence. The relative ease with which the retardant is removed by leaching or laundering necessitates the additional process of coating the fabric with a binding material. Resins may be applied either as emulsions, solutions in organic solvents or as aqueous dispersions. Table 24 summarizes the results of overcoating fabric previously treated with the stannic oxide-phosphoric-tungstic acid retardant system. In a number of cases the glow retardancy of the fabric is destroyed even by the addition of the binder, while in others the resin appears to be inert. Coatings provide various degrees of retardant retention during treatments in detergent media, and their efficiency is best evaluated via the number of launderings

Table 22. Flame and Glow Retardancy in the Three-Component System Including a Phosphate

Bath Concentration %		Temperature Bath No. 2 °C.	No. of Impregnations		Add-On %		Vertical-Bunsen		Flame Test		Horizontal- Microburner	
No. 1	Phosphate		No. 2	No. 2			After- flame sec.	Char Length in.	45°-Microburner After- flame sec.	After- flame sec.	After- flame sec.	Char Area in. ²
$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$			$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$									
12.5	1.0	0	12.5	1	19.8	0	17	4.5	1	10	4.2	5
	$\text{Na}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$											10.7
5.4	4.6	25	5.75	1	13.7	23	2	B.E.*	129	0	B.E.*	0
	$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$											
7.0	3.0	25	10.0	2	31.1	0	7	4.9	17	0	3.2	0
	$\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$											5.1
10.0	3.0	25	10.0	2	44.1	0	8	3.6	0	3	2.5	13
	$\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$											3.5
8.0	3.0	25	8.0	2	31.2	0	7	4.4	2	2	3.7	35
	$\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$											0
												6.3

* B.E.—Burned to the end.

Table 23. The Loss of Flameproofness on Leaching and Laundering Fabrics Containing the Stannic Oxide-Phosphoric-Tungstic Acid Retardant

Solution	Leaching or Laundering Treatment No. of Treatments	Temperature ° F.	Time hrs.	Add-On %		Vertical-Bunsen			Flame Test 45°-Microburner			Horizontal-Microburner		
				Before Treatment	After Treatment	After flame sec.	After glow sec.	Char Length in.	After flame sec.	After glow sec.	Char Area in. ²	After flame sec.	After glow sec.	Char Area in. ²
None	—	—	—	31.2	31.2	0	7	4.4	2	2	3.7	3.5	0	6.3
5% NaCl	1	70	1	31.2	28.7	6	39	B.E.*	6	23	7.2	57	7	B.E.
Running tap water	1	50	72	30.3	28.8	25	88	B.E.	42	89	B.E.	65	10	B.E.
0.5% Igepon-T	1	160	0.5	32.1	28.3	0	7	5.2	39	0	B.E.	60	0	B.E.
0.5% Castile Soap	1	160	0.5	30.8	24.2	27	88	B.E.	46	55	B.E.	74	85	C.B.**
0.2% Na ₂ CO ₃														
0.5% Castile Soap	2	160	0.5	31.2	21.7	29	50	C.B.	44	116	B.E.	74	117	C.B.
0.2% Na ₂ CO ₃														

* B.E.—Burned to the end.

** C.B.—Completely burned.

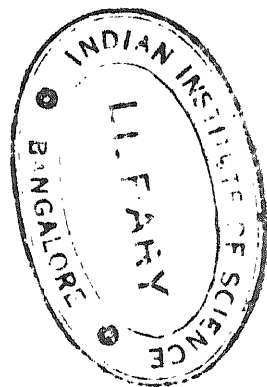


Table 24. The Effect of Resin Overcoatings on the Permanence to Laundering for Fabrics Treated With the Stannic Oxide-Phosphoric-Tungstic Acid Retardant

Oxides and Acids	Add-On %		Total	Resin	No. of Launderings in 0.5% G.I. Soap	45° Microburner Flame Test		Char Area in $\frac{1}{2}$
	Resin	None				Afterflame sec.	Afterglow sec.	
29.0	0		29.0		0	2	2	3.7
23.5	11.0		34.5	Casein	2	44	116	C.B.*
24.5	3.5		28.0	Acetone-Formaldehyde	0	7	215	C.B.
30.0	11.0		41.0	Silica	0	3	686	B.E.**
31.8	4.2		36.0	Merlon IP-40	1	0	278	2.2
31.8	17.1		48.9	Cumar MH2½	0	36	224	B.E.
23.5	4.5		28.0	Urea-Formaldehyde	1	0	27	4.9
38.0	20.5		58.5	Zelan AP-Methacrol BE	1	35	136	C.B.
26.5	5.0		31.5	Phenol-Formaldehyde	0	0	18	2.1
31.8	1.7		33.5	Resloom M-75	3	7	34	2.3
					0	0	0	2.1
					3	1	27	3.4
					0	0	32	3.3
					3	0	30	1.1
					6	39	135	B.E.
					0	0	0	3.1
					6	0	0	2.9
					0	0	0	3.3
					6	0	0	2.0

* C.B.—Completely burned.

** B.E.—Burned to the end.

necessary to cause excessive flaming or glowing. The most efficient of those investigated are the phenolic and melamine types, both of which enable the fabric to withstand 6 standard launderings in "government issue" soap without any detectable loss of protective qualities as measured by the 45° flame test (Table 24). The quantity of the resin coating necessary for this degree of permanence is rather small and does not add materially to the total weight of the treated fabric. This is particularly true for the melamine type which has a further advantage of not appreciably influencing the hand of the treated fabric.

c. Industrial Processing

William P. Hall

The two-bath application of chemicals to textile fabrics may, in general, be divided into two categories: first, application of chemicals which are not substantive, that is, those which do not have a natural affinity for the fibers; and second, application of chemicals which are substantive, that is, those that have a natural affinity for the fibers. The former include ordinary salts such as sodium chloride, potassium sulfate, sodium sulfonated tallow, etc., and the latter direct dyes, cation active softeners and naphthol base salts, etc.

The successful application of substantive materials involves principles of techniques which will not be discussed in this chapter as the chemicals usually employed in two-bath flameproofing processes are not of this type. It may, however, be understood that if non-substantive chemicals are used which react together on the fabric to form an insoluble product, the second material applied may be said in a sense to be substantive since this chemical is removed from the solution by reacting with the chemical already present on the fiber. The second material may therefore be preferentially removed from the second impregnating bath resulting in a gradual decrease in concentration. This is to some extent similar to the conditions obtained when substantive materials are used and the chemicals are preferentially removed by the fibers thus decreasing the concentration of said chemical in the solution.

These principles are important and should be kept in mind when the two-bath methods of application are used since under these conditions the concentration of the second solution must be continually adjusted in order to obtain a uniformly treated fabric. Methods of minimizing and to some extent overcoming these difficulties will be further described.

The application of chemicals to textile fabrics involving two separate impregnations is therefore not difficult provided the two materials do not have a substantial affinity for each other, that is, do not react together quickly to form new compounds. For example, the impregnation with a

hot solution of sodium pyrophosphate followed by drying and impregnation with a cold solution of ammonium phosphate does not represent a difficult problem since the two do not react quickly to form a new compound. On the other hand the impregnation with a solution of soda ash followed by drying and a second impregnation with magnesium chloride is a difficultly controllable process due to the rapid reaction between the two salts.

If the second component reacts with the first to form an insoluble product the relative quantities of chemicals applied should be so adjusted that a minimum quantity of unreacted chemicals remains on the fabric. It is, however, desirable in certain cases where one component has a detrimental action upon the fiber to insure the presence of an excess of the nontendering component. For example, in the two-bath application of zinc acetate and diammonium hydrogen phosphate the latter component should not be present in excess upon the finished fabric since tendering will result during drying and storage. The excess of diammonium phosphate could be removed by cold water leaching, but this would involve an extra operation.

The mechanical operations involved in two-bath applications may for convenience be divided into two systems. First, those in which the fabric passes without drying from one impregnation directly to the second impregnation; and second, those in which the fabric is partially or completely dried between the first and second immersions. Of these methods the one using complete drying is most easily controlled although it cannot be used where the first component has a detrimental degrading effect when dried into the fibers being processed. The wet method and the one using partial drying are more difficult to control, the latter especially, due to the difficulty in adjusting the fabric to a uniform moisture content prior to the second impregnation.

(1) Wet Method of Application

The most widely used method of size application is by impregnation which in this case means bringing the fabric into contact with the solution and then removing the excess by squeezing through two or more rollers. The type of equipment used for this purpose is usually referred to as a mangle or padder and the process as mangling or padding. A mangle may consist, as already stated, of two, three or more squeeze rollers but only the first two types will be discussed here. In the two-roll mangle the cloth is brought into contact with the solution once by using one or more dips and then squeezed, while in the three-roll mangle the fabric may, if so desired, be dipped into the solution twice and squeezed after each immersion. The squeeze rolls may be of rubber, either natural or synthetic, steel, brass, husk or wood, but usually rubber and steel rolls are used.

The solution boxes attached to the mangles may be of any material not

detrimentally reacted upon by the solution chemicals. Stainless steel is usually preferred. The boxes may have one or more dips so that the cloth may be kept in contact with the solution for a short time before the squeezing takes place. This is important especially where heavy, poorly absorbent fabrics are used or where contact between the fabric and the solution for a certain length of time is necessary to allow a reaction to take place such as may occur in the second solution box when the chemicals in the second solution react with those already present on the fabric.

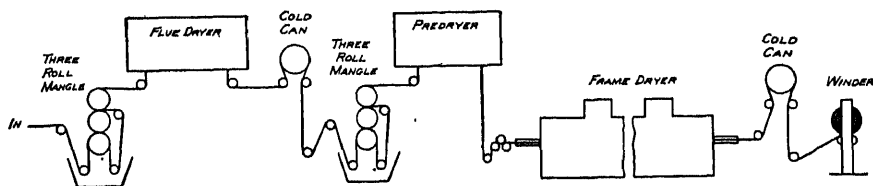


Figure 12. Continuous range for the treatment of fabrics by double-bath processes.

The mangles used in the wet application may be operated separately; for example, the first solution may be applied and the fabric batched in roll form. This wet roll is then taken to a second mangle and the second solution applied. The same mangle may, of course, be used for both impregnations by changing solutions. The process may also be conducted continuously by placing two mangles in tandem and having the cloth pass directly from the first mangle to the second, thus completing both impregnations in one operation.

The squeeze exerted by the two mangles is very important. It is essential that the first mangle exert a heavy squeeze, producing a solution pickup of approximately 50% by weight. The second mangle should then allow an additional 50% pickup from the second bath for a total of 100%. In a process of this type only a short contact with the second solution is necessary in order to obtain the additional 50% solution pickup. It is possible, therefore, to avoid a deep dip into the second bath with the attendant risk of leaching off some of the first component. Contact with the second solution may be accomplished by passing the fabric under a bar just below the surface of the solution or the cloth may pass directly through the squeeze nip. In the latter instance, the lower roll is partially immersed in the bath and serves to bring the solution up to the fabric. In any case, the desired reaction between the two constituents takes place prior to or during drying. From the standpoint of control, this type of application is highly desirable.

As an example of this method, in applying the "Perkin" flameproofing process the concentrations of the sodium stannate and ammonium sulfate solutions are so adjusted that a 50% pickup from each solution assures the proper concentration of chemicals in the cloth. During the subsequent

drying a fine deposit of tin oxide is formed on the fabric leaving only a negligible amount of excess unreacted chemicals.

Another method of wet application may be used with success, provided the chemicals of the first impregnation do not dissolve readily in the second bath but are quickly converted into the insoluble form. It consists in impregnating the fabric with the first solution, using a heavy squeeze if possible, and then bringing the fabric into contact with the second solution for a sufficient time to insure complete combination of the first and second chemicals into the desired compound. The cloth is then finally squeezed before drying. In this case the second bath should be agitated, preferably by an outside circulating pump, to insure uniformity of the solution. A concentrated solution of the chemicals in the second bath should continuously be added into the suction line of the pump and the bath analyzed periodically as a means of maintaining constant composition. This method is not applicable to the Perkin process, where the final insoluble tin oxide is formed during the drying, but only to a process where the final insoluble product is formed in a water medium by precipitation. This method is wasteful since the cloth when leaving the second bath will carry with it a certain quantity of unreacted chemical in addition to that already combined with the chemicals from the first bath.

The equipment used in the final drying operation may be of any conventional textile design such as hot can dryer, flue dryer, loop dryer or frame dryer. Infrared drying lamps or electronic drying may be resorted to but the cost of such methods is prohibitive. In the hot can dryer, the cloth is dried by passing over a series of heated cans; in the flue dryer the cloth passes vertically over a series of rollers inside a drying chamber; in the loop dryer the cloth is hung in a series of loops on bars which move in endless chains inside a drying chamber; in the frame dryer the cloth is held by clips at the selvages under width tension while passing through the drying chamber.

The frame dryer is very desirable since the width of the cloth may be controlled in this machine. Frequently the drying capacity is increased by installing in front of the frame a small number of hot cans or a small flue dryer. This combination constitutes the best equipment available.

The heat may be supplied to these units by steam-heated coils or by direct or indirect gas or oil burners. However, superheated steam coils are the most common source of heat. The cost of electric heating is generally prohibitive.

The temperatures used in the different drying units may vary between wide limits but will usually be between 250° and 350° F. Below 250° F. the drying becomes excessively long and above 350° F. damage to the fabric may result during machine stoppage.

(2) Dry Method of Application

As previously stated, the dry method may be divided into two categories, those in which the cloth is completely dried between the two impregnations and those in which the cloth is only partially dried.

The first method mentioned is the most reliable of all the double-bath processes since it brings the chemicals in the first bath into intimate contact with the fabric by drying them into the fabric. Also, since the cloth enters both impregnating baths in the dry state, the chemical add-on can be carefully controlled in both applications.

The method is limited in its application by the type of chemicals applied. Thus the process is not adapted to compounds having a deleterious effect when dried upon the fibers, or to compounds which alter their character during drying so that the desired combination with the chemicals in the second bath does not occur.

To obtain uniformity it is recommended that the fabric be cooled to room temperature after the first drying. This is done, first, to insure uniform absorbency when immersing in the second bath; and, second, to prevent the hot dry fabric from overheating the second solution, thus causing non-uniform impregnation and possible decomposition of the chemicals in the bath.

The drying equipment used in the intermediate drying may be the same as that used in the final drying as already described.

As previously stated in the discussion of the wet method, the two impregnations and dryings may be conducted in one, two or several steps. As far as labor cost is concerned, the one-step method is the best. The equipment in this case would consist, for example, of a three-roll impregnating mangle, a flue dryer with cooling attachment, another three-roll impregnating mangle and a drying frame all placed in tandem so that the cloth would enter the first mangle dry in one end and emerge from the frame fully impregnated and dried.

The first impregnation and drying could also be conducted in one step followed by another separate impregnation and drying. The slowest method of operation, and therefore the costliest from the standpoint of labor, consists in dividing the process into four separate operations consisting of two steps each of impregnation and drying. This method of production may, however, be improved by using a high speed impregnation mangle feeding two drying units followed by another similar operation.

The use of the semidrying method is the least desirable of the processes so far described. It follows the same procedure as previously outlined except that the fabric is only partially dried after the first impregnation. In practice it is impossible to adjust the residual moisture content with any

degree of accuracy and it therefore becomes difficult to control the quantity of solution picked up in the second bath. If, however, an insoluble compound is formed quickly on the fiber when the fabric is immersed in the second bath and this conversion is complete or nearly so before leaving the second bath, the degree of moisture present after the preliminary drying is of no great consequence. The loss in chemicals from the second solution would however be excessive since the solution carried out by the cloth from the second bath would contain unreacted chemicals.

In most cases the semidry method is used to insure sufficient pickup in the second impregnation. This, however, can also be accomplished as previously described by using the wet method with 50% pickup in the first impregnation and 100% pickup in the second impregnation.

It is possible with the semidry as with the wet method to use chemicals which have a deleterious effect when dried upon the fibers or which are altered during drying, provided the moisture content during the preliminary drying is kept at a certain minimum value depending upon the chemicals in question. This, however, makes it imperative that the drying procedure be run continuously without interruption as any stoppage would completely dry the material in the dryer. This drawback can be reduced to a minimum by good supervision.

The final drying procedure in the dry as well as the semidry method of application is conducted by methods and with equipment previously described.

The two-bath methods described all use an immersion technique in applying the two solutions and this is the most commonly used procedure. It is also possible, however, to apply the solutions by spraying. In this case such difficulties as changes in concentration and composition of the second solution may be eliminated. In some cases both solutions may be applied by spraying or, better still, the first solution is applied by immersion and the second solution by spraying.

The spray method has however some serious drawbacks which make it impractical for large-scale production except in very special cases. These are, first, the penetration obtained is poor, especially in heavy fabrics; second, it is difficult to control the quantity of solution applied and the uniformity of deposit; and, third, the wastage of solution is generally excessive.

The two-bath processes described presuppose the use of aqueous solutions to dissolve or disperse the chemicals. Lately, however, a method has been developed which employs a water-soluble organic solvent medium in the first bath rather than water. This allows the mixing of the two components together with other chemicals in the same solution without the required reactions taking place. The solution is applied by immersion and then usually dried. This is followed by a second immersion in water where the reaction between the two components takes place forming the desired

insoluble product. It is also possible to include in the aqueous second bath additional constituents which contribute to the flameproofing or, as in the case of special resinous treatments, impart a greater degree of permanence to the finish. In like manner, other desirable characteristics such as water repellency may be introduced at this stage of the finishing process.

As an example of this type of process, one of the durable flame-resistant treatments which has been employed commercially in this country¹⁹ makes use of a glycol ether solution of zinc chloride and sodium borate. After immersion in this first bath the deposition of the insoluble reaction products can be achieved by a second immersion in an aqueous medium or by allowing slow hydrolysis and double decomposition to occur in the course of exposure of the treated fabric to humid atmospheric conditions. For practical reasons and to serve as an illustration of the type of process under consideration, it may be assumed that the immersion in the organic solvent solution is followed directly by a second aqueous bath.

This type of flameproofing treatment possesses the disadvantages of increased costs in using an organic solvent in place of water in the first bath and the fact that the regular textile equipment commonly employed commercially is not particularly well adapted to handle organic solvent solutions.

In this section an effort has been made to present the general techniques used in the application of two-bath flameproofing processes. With slight modification either one or the other of these methods may be used depending upon the chemicals and reactions involved. The two-bath methods of obtaining durable or semidurable flameproofing properties have been little used in this country until recently, one reason being the lack of interest and requisition for durable flameproofing finishes. In England, however, the need for such properties in textiles was early recognized and there the two-bath processes have been extensively employed.

3. METALLIC OXIDE-CHLORINATED BODY TYPE

a. Fundamentals of Processes

S. Coppick

The use of metallic oxides alone as fireproofing agents as advocated by Perkin *et al.*^{18,22,23} suffers from several disadvantages. In the first place these treatments are not permanent in the ordinary sense of the word

²² Perkin, W. H., Proc. Eighth Int. Cong. Applied Chem., 28, 119 (1912); Quar. Nat'l. Fire Prot. Assn. 6, 179 (1912); Nat'l. Fire Prot. Assn. Educ. Bul. D 37 (Boston, 1912).

²³ Perkin and Bradbury, Brit. Patents 17814, 17815 (1913); Perkin and Whipp Bros., and Tod, Brit. Patents 9695, 23557 (1901), 6421, 8509, 9620 (1902), 24222 (1903), 22169 (1904).

since they usually lose their retardant qualities fairly rapidly on leaching and laundering. The second disadvantage is the enhancement of the flameless combustion characteristics which the oxides impart to cellulose.

In efforts to offset these features which limit the application of the process, numerous formulations have been proposed for combinations of the metallic oxides with other materials. The function of the extra components is presumed to include the mechanical bonding of the pigment to the fiber, to aid in its practical application, to decrease the abnormal glowing tendencies which accompany the oxide treatment, to improve the hand or color and to inhibit the tendering encountered during weathering or storage. Of the large number of ingredients advocated, the main component appears to be the binder. This is generally a resinous substance which in itself has little or no flaming tendencies and most commonly is either a chlorine addition or substitution product such as polyvinyl chloride, the copolymer of vinyl chloride and vinyl acetate, chlorinated paraffin, diphenyl, naphthalene, or certain halogen substitution products or carbocyclic compounds. The mechanism whereby these materials contribute to the flame and glow-retarding tendencies is assumed to be either in their coating properties to exclude oxygen or their ability to produce hydrogen chloride at flame temperatures to dilute the ambient combustible atmosphere. The combination of the metallic oxide with the chlorinated body is thought²⁴ to be particularly advantageous since the former is presumed to act catalytically as a dechlorinating agent to promote rapid hydrogen chloride production at temperatures in the vicinity of that at which fabric decomposition ensues.

Studies of Individual Components. The system on which the most recent and extensive practical efforts have been directed is that involving antimony oxide and a chlorinated body. It would appear that since this process is of such practical interest and considerable information is available on its industrial application and actual performance, it would be ideal as a basis for fundamental investigations. Such appears to be the case also from an experimental point of view, since the individual components alone appear to be practically inactive in retardant action while certain combinations are very effective. It is therefore possible to study the system without the added complication of varied summative effects.

In fundamental studies on the three-component system: cellulose-antimony oxide-chlorinated body, it is at once apparent that as many as possible of the interdependent variables should be eliminated. Thus application of combinations by direct emulsion or solvent treatments are hazardous since each of the components may influence the state and location of the other. A simpler attack is to apply them separately so that

²⁴ Leatherman, M., Major, C.W.S., Memorandum Report, T.D.M.R. No. 936, Army Service Forces, Office, Chief, Chemical Warfare Service, Edgewood Arsenal, Md. (Dec. 2, 1944).

component and combination effects may be considered on the same basis. This is accomplished conveniently by impregnation of fabrics with the oxide via a dispersion in 2% aqueous methyl cellulose, the binder having been shown to exert an effect similar to an equal added quantity of cellulose itself. The chlorinated body is applied as a solution in an organic solvent such as carbon tetrachloride, trichlorethylene or acetone, and combinations of the two components are added to fabrics both in the above or in the reverse order.

Investigations on the components alone indicate that the antimony oxide has only a slight flame-retarding effect on cotton fabric. Although capable of eliminating afterflaming in the mild vertical test only for very high additions, the oxide exhibits no appreciable retardation of flaming when measured by the more drastic 45° and horizontal testing procedures. Similarly, chlorinated paraffins of various chlorine contents and vinylites have only slight retarding effects when added to fabrics. For the most part they simply reduce slightly the rate at which flame is propagated, as shown in Table 25.

Table 25. The Effect of Various Chlorinated Materials and Their Combinations With Antimony Oxide on the Flaming Characteristics of Fabrics
(Approximately 40% add-on and weight ratios of 1:1)

Retardant Component	Chlorine Content %		Afterflaming (secs.)			Flame Rate in./sec. 45°
			Ver-tical	45°	Hori-zontal	
None	—	—	30	> 60	> 60	0.86
Antimony oxide	0	alone	0	40	> 60	0.57
Pentachlorodiphenyl	54	alone	35	> 60	> 60	0.37
		combined	0	9	> 60	0
Neoprene	40	alone	35	45	59	0.56
		combined	0	1	0	0
Chlorinated paraffin	42	alone	60	> 60	> 60	0.81
		combined	0	0	21	0
Chlorinated paraffin	70	alone	42	> 60	> 60	0.81
		combined	0	0	0	0
Vinylite	50	alone	60	> 60	> 60	0.65
		combined	0	0	0	0
Aniline hydrochloride	27	alone	38	> 60	> 60	0.32
		combined	0	0	0	0

With combinations of the two materials, however, the retardation is very effective. For a given addition of the chlorinated body there exists a minimum add-on requirement of Sb_2O_3 to limit the afterflaming to zero in each of the three flame tests. It is seen further that the relative efficiencies of the chlorinated materials are in direct proportion to their